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PROCEEDINGS

OF THE

CHEMICAL SECTION

OF THE

FRANKLIN INSTITUTE.

(VOL. V.—JAN.-DEC., 1893.)

PHILADELPHIA:

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PROCEEDINGS
OF THE
CHEMICAL SECTION
OF THE
FRANKLIN INSTITUTE.

[*Stated meeting held Tuesday, January 17, 1893.*]

HALL OF THE FRANKLIN INSTITUTE,
PHILADELPHIA, January 17, 1893.

Dr. Wm. H. Greene, President, in the chair.

Dr. Wahl nominated Mr. Joseph Richards, 1802 Catharine Street, Philadelphia, and Mr. Jesse Jones, care of Messrs. Wm. Cramp & Sons, corner York and Thompson Streets, Philadelphia, for full membership in the Section. After action by the Committee on Admissions these gentlemen were declared elected.

Dr. Greene, as chairman of the committee appointed to consider the subject of securing additional papers for the meetings of the Section, made the following report:

"The committee to which was referred the suggestions of Dr. Day that, at stated intervals, reports should be prepared for the Chemical Section on the progress in certain lines of Chemical investigation, respectfully recommends:

"That at every alternate meeting of the Section a conference be given by one of the members, covering the development of some point that may be of general interest to the Section;

"That a committee of three be appointed to serve during the ensuing year for the purpose of securing members or others to give at least five such conferences.

"On inquiry, the committee has found that a number of members are willing to undertake the preparation and presentation to the Section of informal lectures on new developments of the science, and believe that such conferences and general discussion of the subjects considered cannot fail to be of interest to the members, and to increase the attendance at the meetings."

In accordance with this report the President named as members of the committee for 1893, Dr. Wahl, Chairman, Dr. Keller and the Secretary.

The same members as for last year were continued on the Committee on Admissions.

The President appointed Mr. Haines and Dr. Keller members of the Finance Committee.

Dr. Wahl suggested that the Chemical Section might, with advantage to the Institute, exercise the function of securing the lectures on chemical subjects in the general course of lectures annually given by the Institute. He further recommended that the suggestion be left for the present, in order to give time for due consideration by the members with a view of taking official action upon it later in the year.

Dr. Greene then read a highly interesting paper, for himself and Dr. Wahl, on "A New Process for the Production of Manganese on the Commercial Scale."

The paper was referred for publication.

After an animated discussion, partaken in by many of the members present, the Section adjourned. WM. C. DAY, *Secretary.*

PROCEEDINGS.

[*Stated meeting, held Tuesday, February 21, 1893.*]

HALL OF THE FRANKLIN INSTITUTE,
PHILADELPHIA, February 21, 1893

Dr. D. K. Tuttle, Vice-President, in the chair.

A letter from Prof. Henry Trimble was read nominating Mr. Josiah C. Peacock, 3909 North Fifth Street, Philadelphia, for full membership in the Section. As a result of the action of the Committee on Admissions, Mr. Peacock was declared elected.

Dr. Wahl reported that at the special meeting called by the President to consider the adoption of resolutions of respect to the memory of our fellow-member, Dr. F. A. Genth, recently deceased, a committee was appointed to draw up these resolutions, which were published in a number of the leading daily newspapers of Philadelphia. On motion the Section voted that the Treasurer be authorized to pay the bills incurred by the committee in the publication of these resolutions which read as follows:

Resolved, That the members of the Chemical Section of the Franklin Institute have heard with deep regret of the death of their distinguished fellow-member, Dr. Frederick A. Genth, whose eminent services as an investigator have added lustre to American science.

Resolved, That a committee be appointed to prepare a suitable memoir of the deceased for publication in the proceedings of the Section.

Resolved, That as a mark of respect, the Section be requested to attend the funeral in a body.

A paper on "Artesian Wells" by Professor Carter, of the Central High School, was read by title and referred for publication.

Dr. E. H. Keiser, for Miss Mary Bidwell Breed, of Bryn Mawr College, read a paper on "Phenolphthalein and Methylorange." The article was interesting and was well received. Quite an animated discussion as to the relative merits of the two substances as indicators was called forth and was participated in by Mr. Rowland, Dr. Keiser, Mr. Pemberton, Mr. Haines, Dr. Keller and others.

The paper was referred for publication.

Mr. S. W. Young, of Swarthmore College, then made a report of the most important resuls obtained in the field of stereo-chemistry up to the present time. A number of the theories, offered to explain certain interesting cases of isomerism, were stated and illustrated by models showing the supposed special relations of the atoms contained in the compounds considered. The paper was attentively received and on motion the Section voted that it be published in the *Journal.*

Adjourned. WM. C. DAY, *Secretary.*

A NEW PROCESS FOR THE MANUFACTURE OF MANGANESE ON THE COMMERCIAL SCALE.

BY WM. H. GREENE AND WM. H. WAHL.

[*Read at the stated meeting of the Chemical Section, held January 17, 1893.*]

Within a few years manganese has assumed considerable importance as a constituent of several alloys, and the purest manganese of commerce as well as the richest ferro-manganese have been unsatisfactory for the preparation of these alloys by reason of the high proportion of carbon invariably present.

About two years ago we were induced to undertake the search of a process for the manufacture on a commercial scale of metallic manganese that would contain a minimum of detrimental impurities and be absolutely free from carbon. Before describing the process which we have elaborated, we will review briefly the history of the element.

About 1774, Scheele and Bergmann demonstrated that the metallic radical of manganese dioxide is different from iron, and John* isolated the new element by heating a mixture of manganese carbonate and oil, powdering the resulting mass, again mixing it with oil and strongly heating in a brasqued crucible.

St. Claire Deville† modified this process as follows: He reduced pure artificially prepared dioxide to red oxide; mixed this with sugar charcoal in insufficient quantity to reduce the entire quantity of oxide, and heated the mixture in a lime crucible to the highest temperature of a wind furnace.

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* *Gehlen's Jour. Chem. Phys.*, **3**, 452.

† *Ann. de Chimie et de Physique* [3], **46**, 182.

Brunner* heated manganese fluoride, or a mixture of manganese chloride and calcium fluoride, with sodium in clay crucibles.

Giles† prepared a manganese amalgam by the action of sodium amalgam on a concentrated solution of manganese chloride, and expelled the mercury by heating in a current of hydrogen, thereby obtaining pulverulent manganese.

Bunsen‡ obtained deposits of metallic manganese by electrolyzing a concentrated solution of manganous chloride.

The first attempt to produce the metal in considerable quantity appears to have been made by Hugo Tamm§ who in 1872 published the results of experiments made on certain modification of John's method. Native dioxide was reduced by heating with powdered charcoal and oil in the presence of silicious and fluorspar fluxes in graphite crucibles.

The problem presented to us was the reduction of a native oxide of manganese, for it is apparent that the expense of preparation of halogen compounds of the metal and their subsequent reduction would preclude the possibility of applying such a method to manufacturing on a commercial scale.

At the outset of our work it became evident that the first step in the process would be the purification of the ore from iron, which would inevitably be reduced in the reduction of the manganese and could not then be removed from the metal. Magnetic separation appeared to be the cheapest and most effective method, and we made exhaustive experiments in this direction, the ore being treated in all states of division and in all conditions of oxidation, between that of the natural ore and that in which the manganese was reduced to manganese monoxide and the iron to metallic iron. We were compelled to abandon the method entirely, because the iron and manganese are so intimately associated in the ore that no satisfactory separation can be accomplished by the magnet.

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* *Pogg. Annalen*, **101**, 264.

† *Philosoph. Mag.* [4], **24**, 328.

‡ *Pogg. Annalen*, **91**, 619.

§ *Chem. News*, 1872, 111.

We then tried various electro-chemical methods, the ore being made the anode of baths containing sodium chloride solution, ferrous sulphate, dilute sulphuric acid, etc. By such means a certain proportion of the iron may be removed, but the separation is slow, and is far from complete when the manganese oxides begin to be attacked.

Convinced that only a chemical method would answer the purpose, we found after a number of experiments that nearly all the iron can be removed from rich manganese ores by digesting the pulverized ore with about thirty per cent. sulphuric acid near the boiling point, while the manganese is practically unattacked. As an illustration of the effectiveness of the process, we may state that in a few hours the percentage of iron may thus be reduced from five or six to a few tenths, with a loss of not more than one per cent. of the manganese present. The copperas that may be obtained by treatment of the waste acid with scrap iron, will pay the cost of purification of the ore.

The reduction of the ore has been a perplexing problem. While it has never been denied that reduction by carbon in any form yields a metal containing a considerable proportion of the reducing agent, the literature of the subject indicated that this combined carbon might be removed by fusion of the metal under a layer of manganous carbonate or manganous oxide. Thus, Tamm[*] claims to have obtained, from a pyrolusite containing 79·5 per cent. Mn. and 6·5 per cent. F_2O_3, a metal containing

Mn.	96·90
Fe.	1·05
C	0·95
Other elements	1·10

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[*] *Chem. News*, 1872, 111.

and by refining this with manganese carbonate to have raised the proportion of manganese to 99·91 per cent. Other investigators admit the presence of more carbon in the product, but still claim that it may be removed by treatment with manganese carbonate. Our experiments show that the reduction by carbon takes place readily, and only after frequently repeated experiments, in which the proportions of oxide and carbon and the character and proportions of flux employed were varied through wide ranges, did we come to the conclusion that it is impossible by this method to prepare a metal containing less than about six per cent. of carbon, and that it is equally impossible by fusion with an oxidizing agent to remove carbon thus combined with manganese. The results of experiments recently published by Guntz* explain clearly these phenomena. He finds that carbon monoxide is rapidly decomposed by manganese at a red heat, carbon and manganese monoxide being formed. It can then be readily understood why carbon free manganese cannot be made in the electrical furnaces nor in graphite crucibles.

From all these facts we have been led to infer that the reduction of manganous oxide by carbon yields not manganese, but a definite carbide having the composition Mn_3C. We propose investigating this point in the future.

It then became evident that the problem could only be solved by a reduction taking place in the entire absence of carbon. Tentative experiments having given no encouragement to hope that an electrolytic method depending on the decomposition of fused baths of manganese chloride or manganese fluorides mixed with other chlorides and fluorides could be devised, the only alternative became a purely chemical process, the details of which were worked out during the progress of the laboratory work. The importance of these details will become apparent as we describe the steps of our process.

The pulverized manganese ore purified from iron, or containing less than one per cent. iron, is exposed to the action of reducing gases at a temperature approximating redness. All the manganese is thus converted into greenish-grey manganese monoxide, which must be allowed to cool out of contact with air to prevent oxidation to red manganoso-manganic oxide.

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* *Comptes Rendus*, **114**, 115.

The monoxide is then mixed with about eighteen per cent. of its weight of granulated aluminum and a suitable flux and the mixture is heated to a temperature near the melting point of cast iron in magnesite crucibles. The flux may be silicious or a mixture of lime and fluorides, or lime alone. As soon as the temperature of reaction is attained the mass promptly fuses and must be poured from the crucible while at its maximum temperature. While the character of the flux has little influence on the reaction, it has important relation to the yield and quality of the metal obtained. A silicious flux naturally occasions the introduction into the manganese of a certain proportion of silicon. If the flux be too fusible a quantity of the aluminum may rise to the surface and escape the reaction. A mixture of lime and fluorspar has given us the best results in crucible operations.

Theoretically, one part of aluminum should yield three parts of manganese; the best results we have obtained on the small scale, producing several pounds of manganese at one operation have given us two and eight-tenths parts or ninety-three per cent. of the theoretical yield, and our average yield has been about eighty-seven per cent. With aluminum at its present price we therefore estimate that the absolute cost of producing carbon-free manganese containing, Mn ninety-six to ninety-seven per cent., Fe and Si each one to two per cent., by our process, will be within thirty-five cents a pound, this estimate including all expenses.

On the large scale we purpose conducting the operation on a magnesite lined hearth, reducing gases being in slight excess. By this means we believe that the manganese will be retained in the state of lowest oxide until the temperature of reaction is reached, and that the prompt fusion of the flux at this stage will protect the manganese formed from contamination by carbon from the flame.

We may mention in conclusion that having experienced considerable difficulty in obtaining and preparing magnesite crucibles, we adopted the expedient of lining plumbago crucibles with a stiff paste of calcined magnesite. When properly prepared, these linings do not crack on drying, and do not shrink from the plumbago walls. After thorough drying, the crucibles are ready for use, and we have found the linings very serviceable, not only for the preparation of manganese, but in other metallurgical work in which silicious or plumbago crucibles were from any cause objectionable.

PROCEEDINGS.

[*Stated meeting, held Tuesday, March 21, 1893.*]

HALL OF THE FRANKLIN INSTITUTE,
PHILADELPHIA, March 21, 1893.

Dr. Wm. H. Greene, President, in the chair.

The special committee appointed to prepare a memoir of the late Dr. F. A. Genth presented, through Dr. Keller, an elaborate paper, embodying an account of the life and scientific work of the deceased, including a complete list of all the papers published by him. The paper was referred for publication in the *Journal of the Institute*, and on motion the committee was discharged, with the thanks of the Section for the thorough manner in which it had discharged its duties.

A letter of resignation from Mr. A. T. Eastwick was read, and on motion the resignation was accepted.

A bill amounting to $38.38 from the Institute for expenses of postage, etc., incurred in connection with sending out notices, and for the work involved in the separate binding of the volumes of Proceedings for 1892, was read, and on motion was referred to the Treasurer for payment.

Dr. Wahl, as conservator of the Section, reported that he had in his possession fifty-two copies of vol. i, ninety-seven copies of vol. ii, eighty-two copies of vol. iii, and forty-five copies of vol. iv of the Proceedings of the Section, and in reply to his inquiry as to what disposal should be made of them, the Section voted to leave them in his hands to dispose of in the interests of the Section in such manner as his judgment might dictate.

Dr. Wahl then read a paper, which was the joint production of himself and Dr. Greene, on a "New Method of Reducing Metallic Oxides."

It was received with much interest by the members present, and after some discussion by Dr. Hall and Dr. Wahl was referred for publication. Specimens of the products of the process were exhibited.

The Section then adjourned. WM. C. DAY, *Secretary.*

ON PHENOLPHTHALEIN AND METHYLORANGE AS INDICATORS.

BY MARY BIDWELL BREED.

[Read at the stated meeting of the Chemical Section, held February 21, 1893.]

In using phenolphthalein as an indicator in alkalimetry, there are certain precautions necessary that have not been sufficiently insisted upon in the literature of the subject. The following experience, however, will show the necessity for great care in its use.

During the standardization of a hydrochloric acid solution against normal caustic potash, phenolphthalein and methylorange were both used as indicators; and it was observed that, while with methylorange 20 cc. of the acid required only an average of 19·443 cc. of the alkali for neutralization, with phenolphthalein the same amount of acid required an average of 19·765 cc. of alkali, a difference which would introduce a considerable error. The same results were obtained with phenolphthalein, even when the solution was heated to boiling, and so it was believed that carbon dioxide could not be the cause of the discrepancy. That the source of the difficulty lay with the phenolphthalein, and not with the methylorange, seemed probable from the fact that it took more alkali to bring the color of phenolphthalein than to discharge that of methylorange; and also from the fact that, while the amounts of alkali used with the former varied from 19·65 cc. to 19·8 cc., those used with the latter were practically constant, differing only by 0·025 cc. Nothing could be found in the literature of the subject that threw any light on the problem. Fresh solutions, prepared with great care, gave analogous results, and after many fruitless attempts to explain the discrepancy, it was concluded that traces of carbon dioxide, dissolved by the alkali, must after all be the source of error. This would explain matters; for acid potassium carbonate, which would be formed in the solution during titration, is neutral to phenolphthalein, but alkaline to methylorange; and, therefore, as part of the alkali had been rendered neutral to phenolphthalein, it would take more of the solution to affect that indicator than to affect methylorange. This explanation was proved to be correct by prolonged, hard boiling of the solution, when using phenolphthalein. Alkali was titrated with acid, in this case, and it was found that, by boiling ten minutes or so after the end point had been apparently reached, the color could be made to reappear, and that it continued to reappear after each addition of acid until the amount of acid used was exactly equal to that used with methylorange. As the end point was approached, longer and longer periods of boiling were necessary after each drop added. A single titration never took less than an hour.

In view of this, a word of caution seems necessary. It is never safe to use phenolphthalein unless the solution is known to be absolutely free from carbon dioxide, or unless it is boiled long and thoroughly after the end point is apparently reached. As it is nearly impossible to keep a solution of caustic alkali entirely free from carbon dioxide, a titration with phenolphthalein is often as tedious as a gravimetric determination.

Phenolphthalein is probably used at present more extensively than any other indicator, but these objections make it desirable to adopt something more reliable and convenient, Methylorange is not affected by carbon dioxide, and when a sufficiently dilute solution is used, its end point is sharp. It has been found very satisfactory for sensitiveness and accuracy, and it is therefore strongly recommended whereever it is possible to use it.

CHEMICAL LABORATORY,
BRYN MAWR COLLEGE, PA., January, 1893.

DISCUSSION.

MR. HAINES suggested that the glass beaker may have been attacked by the boiling alkaline solution, resulting in extraction of alkali from the glass, especially if the boiling was continued as long as an hour. Such action has been observed even with Bohemian glass. The glass is stated to be generally attacked as a whole. As regards phenolphthalein and methylorange he wished to call attention to the statement by R. T. Thomson, in his comprehensive papers on indicators (*Chemical News*, **47,** 123, 184, and **44,** 32, 38, 119), that phenolphthalein has five times greater delicacy or sensitiveness than methylorange. In other words, in 100 cc. of distilled water, the former requires but 0·1 cc. of excess of deci-normal solution, while the latter requires 0·5 cc. of excess to produce the full change of color. In solutions of normal strength the difference is scarcely noticeable. He showed that this difference was not due to carbonic acid, but to the interference of neutral salts of sodium potassium, and ammonium formed during tritration, which affect the delicacy of methylorange, but not phenolphthalein, except in the case of salts of ammonia. Neutral salts of calcium, barium and magnesium have the same effect upon methylorange. Mr. Haines said that in recently making some determinations, requiring the use of both of these indicators, he had found the above statement as to this difference to be correct. A fresh standard solution of sodium hydrate, made from metallic sodium and carefully protected, gave practically the same results as an old solution of ordinary sodium hydrate in white sticks. In determining alumina volumetrically in sodium aluminate by the method described by Lunge (*Jour. Soc. Chem. Industry*, 1891, p. 314), in which both indicators are used and the amount of alumina is calculated from the difference of results of titration, Mr. Haines obtained results which agreed very closely with gravimetric estimations in the same solutions if the above correction for difference in delicacy of indicators was applied. Generally, methylorange is used only in a cold solution, but Lunge has shown that in estimating alumina volumetrically with methylorange, the solution should be heated to 30° to 40° C., but not exceeding the latter temperature. The action in the cold solution is too slow and the alumina is apt to be underestimated. Only dilute solutions of alumina should be used.

Phenacetolin also is a more delicate indicator than methylorange, being similar in this respect to phenolphthalein. In estimating calcium, magnesium and sodium carbonates, as in Hehner's method of determining hardness of waters, Mr. Haines has found, as others have also, that phenacetolin is preferable to methylorange, but in this case the former must be used hot, the latter cold. He finds that the alcoholic solution of phenacetolin keeps very much better if it is not filtered from the insoluble residue found in the article as sold.

Mr. Haines has also experienced some difficulty in obtaining the true methylorange (helianthin). Sutton incorrectly describes it as of a bright orange-red color; Allen states it is orange-yellow. An article of bright orange-red color sold in this country as methylorange gave the *reverse* of the correct colors with acids and alkalies and was so wanting in delicacy as to be practically worthless.

The article recently obtained from Bullock & Crenshaw, which agrees nearly with Allen's description, he had found to be perfectly satisfactory.

MR. HENRY PEMBERTON, Jr., remarked that in titrating with phenolphthalein and with methylorange as indicators, different results would be obtained if the standard alkali contained alumina. This impurity is not infrequently present in sodium or potassium hydrate. Even a small amount of alumina [*about* 0·002 grams] will require when methylorange is used 1 cc. of $\frac{N}{10}$ acid more than when phenolphthalein is used.

In regard to titrations with phenolphthalein in the presence of ammonium salts, J. H. Long has shown* that correct results are obtained when the solution is kept cold, and a sufficient quantity of the indicator is employed.

PROF. E. S. KEISER, in reply to Mr. Haines, said that while according to R. T. Thomson, methylorange was not as sensitive as phenolphthalein, other observers had found it to be more sensitive. For example, J. Wieland (*Berichte d. Deutschen Chem. Gesell.*, **16**, 1989), found that from three to four times as much of a $\frac{1}{100}$ normal solution was required to bring about the change of color with phenolphthalein as with methylorange. That is the phenolphthalein is less sensitive than the methylorange. Experiments made in the speaker's laboratory indicated that methylorange when used in the proper dilution was fully as sensitive as phenolphthalein. The great objection, however, to the use of phenolphthalein in ordinary titrations is its sensitiveness to carbon dioxide, and that it is neutral to acid carbonates. For example, R. B. Warder (*American Chem. Journal*, **3**, 55) has shown that alkaline solutions of this indicator can be decolorized by shaking them with air, and that by simply breathing upon the red liquid the color is discharged. The phenolphthalein is not colored by acid carbonates. Mr. Haines would find in the paper by R. T. Thomson, to which he refers, that that author distinctly states that when alkaline hydroxides containing alkaline carbonates are titrated and phenolphthalein is used as indicator, the color disappears when the hydroxide is neutralized and the carbonate changed to acid carbonate. That if the solution is then boiled the color reappears because the acid carbonate is decomposed, and more acid must be added and the titration continued until the color no longer appears in the boiling solution.

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* *American Chemical Journal*, **11**, 84.

As it is almost impossible to prevent standard alkali solutions from absorbing carbon dioxide from the air, it is evident that the strength of such solutions will constantly change if the determinations are made with phenolphthalein as the indicator. On the other hand, if the titrations are made with methylorange as the indicator the results are in no way influenced by the amount of carbon dioxide that has been absorbed. Hence, in all ordinary work it is advisable to use methylorange.

[*Proceedings of the stated meeting, held Tuesday, April 18, 1892.*]

HALL OF THE FRANKLIN INSTITUTE,
PHILADELPHIA, April 18, 1892.

DR. WM. H. GREENE, President, in the chair.

The Section met at the usual hour. A number of bills, for subscriptions to journals and expenses incurred by the Actuary in mailing the Section's notices and papers, were approved for payment.

An interesting paper, by Dr. Edgar F. Smith and Mr. Vickers Oberholtzer, on "The Action of the Haloid Acids in Gas Form upon Molybdic Acid," was read by Dr. Smith, and was referred for publication.

Adjourned. H. PEMBERTON, JR., *Secretary pro tem.*

[*Proceedings of the stated meeting held Tuesday, May 16, 1893.*]

HALL OF THE FRANKLIN INSTITUTE,
PHILADELPHIA, May 16, 1893

DR. WM. H. GREENE, President, in the chair.

A letter from Mr. F. A. Genth, Jr., acknowledging the receipt of the memoir of the late Dr. F. A. Genth, was read, and in response to a question contained therein relative to the embodiment of the Section's memoir in another to be prepared by the family, it was voted that the paper could be used in any way desired by the relatives of the deceased.

On motion of Dr. Hall it was voted that the *Zeitschrift für Anorganische Chemie* be added to the list of journals subscribed for by the Section.

Dr. Tuttle read a paper on "a process of treating mixtures containing sulphides of precious metals and copper." After the conclusion of the paper he called attention to the patented process of dissolving gold, etc., in a dilute solution of potassium cyanide. An animated and interesting discussion of the questions treated of by the author followed, and was participated in by Dr. Keller, Dr. Hall, Mr. Pemberton, Dr. Greene and Mr. Phillips. The paper was referred for publication.

Dr. Tuttle suggested as a good subject for investigation the action of sodium sulphide on silver in presence of water entirely freed from dissolved oxygen, with a view to detecting hydrogen, which, under the circumstances named, should be evolved if the usual action of a solution of sodium sulphide on silver takes place.

Professor Smith then read a paper by himself and Mr. Victor Lenher on "the action of ammonia gas upon molybdenylchloride." The paper was briefly discussed by the author and Dr. Tuttle and was referred for publication.

Dr. Wahl called attention to some samples of an abrasive material known as carborundum, made by subjecting a mixture of silica and coke to the heat of an electrical furnace. The material is a good substitute for emery and corundum, and even for diamond dust in polishing diamonds.

Dr. Keller followed with a conference on "Recent Contributions to our Knowledge of Metallic Reducing Agents." The subject was most admirably presented and called forth a vote of thanks. It was referred for publication in the *Journal.*

The Section then adjourned. WM. C. DAY, *Secretary.*

A MEMOIR OF FREDERICK AUGUSTUS GENTH.*

FREDERICK AUGUSTUS GENTH was born May 17, 1820, at Waechersbach, in Hesse-Cassel, where his father occupied the position of "Forstmeister" to Prince Isenburg. He received his early training in the gymnasium at Hanau. His university studies began at Heidelberg. While there, although he exhibited much interest in mineralogical and chemical studies, and made frequent botanical and geological excursions, he does not appear to have definitely decided upon his future career. His earliest papers, which he published in 1842, while still a student, in Leonhard-Bronn's *Jahrbuch*, were upon subjects having reference to conchology, geology and mineralogy.

From Heidelberg he proceeded to Giessen, where the fame of that greatest of all teachers of chemistry, Liebig, was attracting students from all parts of the civilized world. There were assembled around this master many men whose names have since become illustrious in chemistry.

When Genth entered the Giessen laboratory, he met among others the two assistants, Fresenius and Will, and as fellow-students with such men as Hofmann, Wurtz, Strecker and Varrentrapp.

The master mind of the head of the laboratory and the scientific atmosphere of the place, had doubtless a great influence upon the young student, and gave his studies a definite direction; but it was under the guidance of Fresenius that he began his chemical exercises. In later years,

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* Report of a Special Committee of the Chemical Section. Read and accepted at the stated meeting held March 21, 1893.

Genth was wont to express his indebtedness to this great analyst for having laid the foundation of what was later to become the field of his principal scientific work.

At the same time, however, he continued zealously to cultivate the mineralogical studies, and he seems to have given special attention also to crystallography. * * *

Under Liebig's direction he made and published a chemical investigation of a new resinous body, which was given the name of masopin.

In 1843, he went to complete his university studies with Bunsen at Marburg. This eminent savant also had surrounded himself at this time with a circle of students, many of whom afterwards became famous. Among these appear the names of Kolbe, Frankland and Tyndall.

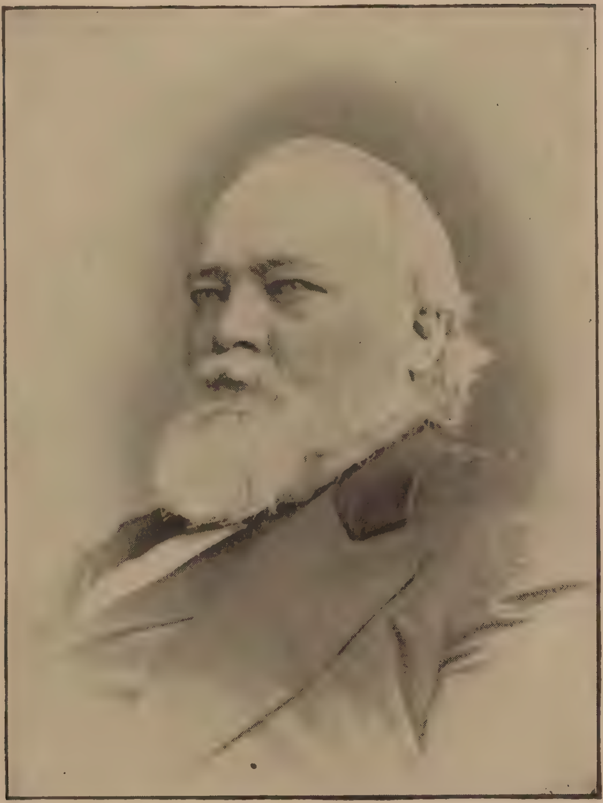
For three years he acted as Bunsen's assistant. His contributions to science during that time were numerous: a few of these related to geology, most of them, however, were on mineral-analytical subjects. The most important of the latter was an investigation of the metallurgical process of the Friedrichshütte near Riechelsdorf.

The results of this well-known research were embodied in the dissertation, which, in 1846, he submitted to the Philosophical Faculty of Marburg, which conferred upon him the degree of Doctor of Philosophy, after he had passed the required examination with high honors. * * *

In the following year, 1848, having meantime married, Genth came to this country. He took up his residence in Philadelphia, and here established an analytical laboratory. Most of his time was taken up with commercial work and with the instruction of young men. His leisure he devoted to original research. Thus he was occupied for more than twenty years.

In this time not less than fifty-six contributions from his pen have appeared, with notable regularity, in various scientific journals. His earlier papers appeared in Keller & Tiedemann's *Nordamerikanischer Monatsbericht* and the *Proceedings* of the Academy of Natural Sciences. His later work was published in the *American Journal of Science*, and several important communications appear in the *Journal of the Franklin Institute.*

Jour. Frank. Inst., Vol. CXXXV. June, 1893.



FREDERICK AUGUSTUS GENTH.

(1820–1893.)

He held, for many years, the post of chemist to the State Board of Agriculture of Pennsylvania, being the first to be elected to this office, and practically controlled the fertilizer trade of this State. One of the most prominent specialists in this branch of manufacture bears testimony that his official work was always regarded as being absolutely reliable. This position he held until the recent establishment of the Agricultural Experiment Station in connection with the State College, to which was transferred the conduct of all researches in the interests of agriculture.

He was also, for a number of years, mineralogist to the Second Geological Survey of Pennsylvania.

In 1872, he was elected to the chair of chemistry and mineralogy at the University of Pennsylvania. This position he held until 1888, when differences with the administration caused his withdrawal.

He was the recipient of many evidences of appreciation of his scientific work. He was a member of the National Academy, President of the American Chemical Society, and Honorary Fellow of the American Association for the Advancement of Science. For many years he was an active member of the Academy of Natural Sciences and of the Franklin Institute. He was an honorary member of our Section.

Notwithstanding the distractions of commercial work, to which he was compelled to devote much of his time, and, later on, those of a laborious professorship, he was able, thanks to his unflagging scientific enthusiasm and enormous capacity for work, to contribute more than one hundred papers embodying the results of his personal observations and researches during his professional career of about half a century.

In placing an estimate upon the scientific career of the subject of this memoir, it is not too much to say that he was one of the ablest mineralogists, and certainly the foremost mineral analyst this country has known.

His scientific labors embrace mineralogical, geological and chemical subjects, but valuable as are the results of his chemical researches, his fame will rest chiefly upon the contributions he has made to our knowledge of the minerals of this country. His name appears on almost every page of the records of mineralogy.

His innumerable observations and his careful analyses have helped to throw light upon every class of mineral species. Of the more than one score of well-established species which he added to the list of our minerals, we need only mention a few, such as nickel gymnite (named genthite by Dana), whitneyite, cosalite, coloradoite, psittacinite, aguilarite, calaverite, lansfordite and nesquehonite; but he deserves no less credit for the elimination of doubtful species and the characterization of others that had been imperfectly described.

In connection with his work in this direction, we should not omit to notice the elimination of owenite, harrisite, coracite, cherokine, and Endlich's schirmirite, and his characterization of roscolite, hiddenite and herderite. His most important contribution to mineralogy is probably his monograph on *Corundum: Its Alterations and its Associated Minerals*. His ingenious interpretation of the metamorphoses exhibited by this mineral, upon which, as well as his numerous careful analyses, his conclusions as to the character of the alterative operations of nature were based, have now been generally accepted by mineralogists and geologists.

His preliminary report, on the mineralogy of Pennsylvania, is an invaluable guide to the mineral history of the State, and the same may be said of his report on the minerals of North Carolina.

His contributions to chemistry proper are less numerous, though some are of considerable importance. In this category undoubtedly must be placed his famous discovery of the "Ammonia-Cobalt Bases," the credit of which, certainly belongs to him, notwithstanding the almost simultaneous announcement of those compounds by Claudet and Frèmy. The joint investigation of these compounds by Gibbs and Genth is a classic research.

His much-quoted paper, on "The Metallurgical Process of the Friederichshütte," is replete with interesting results, notable among which is the discovery of an allotropic form of oxide of nickel contained in the metallic copper. Familiar to all the analytical fraternity is his method of analyzing chrome iron ore and his method of determining copper as oxide.

As a teacher Genth possessed, in a remarkable degree, the ability to impart knowledge. His method consisted substantially in inducing the student to cultivate the habit of close observation and reasoning rather than that of committing facts to memory. Many of his students have attained to positions of distinction, and will be able worthily to perpetuate his fame.

The personal character of the man could almost be predicted by those who never enjoyed the privilege of his acquaintance and friendship, from the sterling character of his scientific work.

He had in full measure the typical characteristic of the German nature, in his love for thoroughness and contempt for superficiality and sham. He was unaffected in manner, and though at times he may have exhibited a certain brusqueness even towards his friends and intimates, this eccentricity served only to attach them more closely to him. To them he was thoroughly devoted, and those who knew him best loved him most. His friendly interest in young men about beginning a scientific career exhibited one of the most charming traits of his nature, and the writers of these inadequate lines which they affectionately dedicate to his memory, gratefully recall from earlier days, the acts of considerate kindness and words of encouragement of the revered master whose life work is done.

His private life was blameless, and in his domestic relations, which were most happy, he was a devoted husband and father. He was twice married, and three sons and five daughters survive him.

WM. H. WAHL,
HARRY F. KELLER,
T. R. WOLF,
Committee.

A NEW METHOD OF REDUCING METALLIC OXIDES.

By Wm. H. Greene and Wm. H. Wahl.

[*Read at the stated meeting of the Chemical Section, held Tuesday, March 21, 1893.*]

In a previous paper by ourselves, presented at the January meeting of the Section, we gave an account of the various methods that have been proposed for the production of metallic manganese, and described a method which we had devised for the production of this metal, and which we believe to be adapted for commercial use, based on the reduction of one of the lower oxides of manganese by means of aluminum.

In the search for commercially available reducing agents applicable to the solution of the manganese problem we gave consideration to all the elements of which the known thermo-chemical data gave us reason to hope for an exothermic reaction with the oxides of manganese.

Among these silicon did not escape our observation, inasmuch as the heat of formation of its oxide SiO_2, according to the most reliable estimates, is sufficiently greater than that of $2MnO$ to permit us to expect that the desired reaction should take place.

The references in the literature of chemistry to the reducing action of silicon are not numerous. The only investigations that appear to have a direct bearing thereon are those of Gore,[*] who makes the observation that "crystals of silicon thrown upon melted argentic fluoride become red hot, undergo rapid combustion, forming fluoride of silicon and depositing silver." By adding crystals of silicon to melted black oxide of copper, the same author[†] observed a sudden incandescence which raised the temperature to full white heat; copper was also deposited and melted to a red metallic bead and could be hammered to a thin sheet. He noted also that crystals of silicon immersed in a solution of fluoride of copper, containing free hydrofluoric acid, instantly coat themselves with bright copper, and that when silicon is thrown into melted fluoride of sodium, bubbles of vapor are evolved which explode and burn with a yellow flame at the surface of the liquid. The silicon was found subsequently to have lost in weight.

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[*] *Chemical News*, **29**, 291.

[†] Gore, *The Art of Electro-metallurgy* (1877), p. 220.

More recently Warren* has published an account of a number of instructive experiments, which strikingly illustrate the energetic reducing properties of silicon. He notes the fact that metallic silicon, though a very stable and inert substance, yet when in admixture with a large number of metallic oxides, becomes at once oxidized, the oxide in admixture with the same becoming itself reduced. Litharge, for example, when mixed in excess with silicon and heated to dull redness, becomes reduced to metallic lead. With copper and all other readily reducible oxides, either a silicide, or, when the oxide is in excess, the pure metal is obtained. He observes that even the oxides of chromium, tungsten and molybdenum are reduced to the metallic state when heated with silicon.

The fact that silicon in the elementary form can only be obtained by indirect and costly methods, rendered any serious consideration of its availability for our purpose out of the question. The thought presented itself, however, that compounds of silicon might possibly be found to answer our purpose, and a very slight consideration of the subject encouraged us to believe that in the metallic silicides we had at hand a ready means of utilizing the chemical energy of one of the most powerful reducing agents.

It appeared reasonable to conclude also that the reducing power of such silicides might be found serviceable not only in the reduction of the oxides of manganese, but also in the reduction of many other metallic oxides.

Certain facts in connection with the metallurgy of steel and copper when given their proper interpretation appeared to strengthen this view. Thus, in one of the modifications of the open-hearth process of steel making, in which pig iron and scrap are melted on the hearth in contact with oxides of iron, not only the greater part of the carbon but also practically all of the silicon which is invariably present in small proportion is eliminated from the resulting steel, by the reaction with the oxides of iron, and finds its way into the slag as silicate.

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* Warren, *Chemical News*, **65**, 75.

Also, in the commercial operations of reduction, remelting and casting of certain metals and alloys, serious practical difficulties arise from the formation or retention therein of small quantities of oxide which have an unfavorable influence upon the strength, ductility and other desirable properties of the metals and alloys, and often render it troublesome to roll them or to obtain sound castings from them.

To counteract such difficulties, compounds in which silicon is present have come into use, either for the purpose of prevention or correction. We may refer as illustrations to the use of ferro-silicon in foundry practice and in the open-hearth process, and to the suggested use of copper, tin and zinc silicides to copper, tin and zinc and their alloys, all for the same general purpose of insuring the production of homogeneous metal and sound castings. In these cases the utility of the silicon appeared to us to be due manifestly to its energetic reducing action on the minute quantities of oxides retained in the molten metal, and to be strictly comparable to the action of phosphorus, magnesium, manganese, aluminum and other energetic reducing agents employed in the purification or refining of metals from small quantities of retained oxides.

Having satisfied ourselves from preliminary considera-ations of this nature that the use of silicon in the form of the metallic silicides might hopefully be applied as the basis of a commercial method for the reduction of oxidized ores of the metals, we proceeded at the first opportunity to make a number of experiments to test the correctness of our reasoning.

The requirements of iron founders and steel makers, we found, had caused a considerable demand for pig irons containing relatively high proportions of silicon. These are known to the trade as ferro-silicon, silico-spiegel and silico-ferro-manganese, the last two being so designated from their manganese content. These products may be described as silicides of iron, or of iron and manganese, containing from five to thirty per cent. of silicon, and a relatively low percentage of carbon. These silicides seemed adapted to our purpose.

We will confine ourselves here, for convenience, to the description of our method as applied to the production of ferro-alloys. It is obvious that in the production of such alloys, which, if useful at all, will find their principal application in the manufacture of special steels, the presence of carbon in notable proportion will be highly detrimental.

For this reason we require for our purpose a silicide containing as high a proportion of silicon and as low a proportion of carbon as possible. Silicon irons and spiegels containing as high as fifteen per cent. or twenty per cent. of silicon and with carbon not exceeding one per cent. can readily be obtained, and, as we are assured, by special selection of ores and fluxes, can be supplied on demand even higher in silicon than the figures just named. It is interesting also to note the fact that, as a rule, the quantity of carbon, in such silicides, varies with the silicon in an inverse ratio, the carbon decreasing as the silicon increases, and *vice versa.*

We may fully illustrate our method by describing its application to the production of a ferro-manganese; the object in view being substantially the manufacture directly from the oxide of a ferro-alloy sufficiently high in manganese and at the same time sufficiently low in carbon that it may be employed with economic advantage in the production of manganese steel, the deoxidation of the charge in the Bessemer converter, or on the open hearth.

The possible utility of the method may most strikingly be illustrated with reference to the ultimate production of manganese steel, an alloy that is known to possess certain unique and highly desirable qualities, but which presents certain practical difficulties in its manufacture in large quantities which thus far have proved to be troublesome.

By the way of explanation it should be stated that by the present method of manufacturing this alloy, which consists substantially in the addition of ordinary ferro-manganese to fluid iron, the proportion of manganese that can usefully be introduced into the steel is rigorously limited by the carbon, which to the amount of 5 to 6 per cent. is present in the ferro-manganese and which cannot be eliminated therefrom because of its affinity for manganese.

With this explanatory comment we proceed to describe the production of a ferro-manganese by the method which we propose. The chemistry of the operation is extremely simple. When a ferro-silicon (or other silicide) is heated in any suitable furnace chamber (which for our purpose is preferably lined with basic material, such as lime or magnesia) in contact with a metallic oxide (or a mixture of such oxides) and in the presence of a suitable base, such as lime, magnesia, or alumina, the oxygen of the oxides combines with the silicon forming silica, which at once unites with the base to form a more or less fusible silicate that separates as slag, while the metals set free combine to form an alloy.

The mode of our procedure is, precisely stated, as follows: We select a terro-silicon or silico-spiegel adapted for our purpose and melt the same on the hearth of a furnace, or in a crucible. Then the manganese monoxide (or the proto-sesqui oxide) with which a fluxing material has been incorporated is added in proper quantity. The reaction takes place promptly, the silicon of the ferro-silicon seizes upon the oxygen of the manganese ore, and is thereby converted into silicic oxide which forms with the flux a liquid slag, while the manganese set free by the reduction of the ore combines with the molten iron set free from the silicide. The whole charge of manganese and flux may be added to the ferro-silicon at once, or the addition may be made by portions until a sufficient quantity of the oxide has been employed to utilize the reducing power of all of the silicon that was present in the ferro-silicon, thus reducing a chemically equivalent quantity of manganese oxide to the metallic state.

Assuming that we operate with a silicide containing iron

88 per cent., silicon 10 per cent., carbon 1 per cent. The reaction for simplicity's sake may be supposed to take place according to the equation

$$2\ MnO + Si = SiO_2 + 2\ Mn.$$

We would then employ silicide and manganese oxide in quantities that satisfy the above proportions, *i. e.*, for every 28 parts of silicon in the silicide 142 parts of manganese monoxide and a quantity of lime, manganese or alumina, or a mixture of these that will completely combine with the silicate to form a fusible silicate.

It is necessary, of course, to use a larger quantity of manganese ore than that required by theory, for the reason that a certain quantity of the manganous oxide is always seized upon by the silica and passes into the slag in the form of manganous silicate.

A charge of ferro-silicon (containing 10 per cent. silicon, 1 per cent. carbon) 100 pounds, manganese monoxide 70 pounds, lime 50 pounds, we have found to yield about 128 pounds of a metallic alloy having the composition: iron 70 per cent., manganese 29 per cent., carbon 0·7 per cent., silicon trace.

Assuming that the permissible percentage of carbon in a certain manangese steel is 0·5 per cent., then 100 pounds of a manganiferous alloy of the above composition will produce by mixture with 40 pounds of decarburized iron, 140 pounds of manganese steel of the composition iron 78·8, manganese 20·7, carbon 0·5, silicon trace.

In the preparation of a manganese steel containing the same percentage of carbon by melting decarburized iron with ordinary ferro-manganese containing 80 per cent. manganese and 5·5 per cent. carbon, the resulting metal would contain 92·23 per cent. iron and only 7·27 per cent. manganese. Or, making the comparison on the basis of equivalent quantities of manganese, the manganese steel made from the ordinary ferro-manganese would contain for 20·7 per cent. manganese, 1·4 per cent. carbon; that made by our process would contain for 7·27 per cent. manganese only 0·18 per cent. carbon.

In many cases it is obvious that a metal of the desired composition may be obtained directly by one operation on the furnace hearth. It is probable, for example, that for the production of a manganese steel of a given composition, the required proportions of scrap wrought iron and ferro-silicon of suitable composition could be melted on the hearth, in contact with the manganous oxide.

By procedures substantially like that described, but substituting for the manganous oxide, oxides of nickel, chromium and tungsten, we have succeeded in forming ferro-alloys of nickel (containing as high as 50 per cent. of this metal), chromium (with nearly 20 per cent. of chromium) and tungsten (with more than 50 per cent. of tungsten). With titanium, we have thus far obtained only doubtful results. In all these cases the resulting ferro-alloy is relatively low in carbon, and, as the method we propose does not involve the introduction of carbon either as the reducing agent, or from external sources, the carbon in the product being derived wholly from that which is contained in the ferro-silicon employed in the operation, we have reason to believe that we will be able to produce, on the commercial scale, ferro-alloys with any desired metals so low in carbon as to meet all the requirements of the metallurgical arts.

Thus far our experiments have been confined to the ferro-alloys and have been on the laboratory scale. It will be obvious, however, that the chemical reactions involved will hold good for other classes of alloys, and that alloys of copper, for example, with difficultly-reducible metals, may be obtained quite as readily by fusing the appropriate oxides with copper silicide.

In conclusion, the method which we propose, we believe, will enable the metallurgist advantageously to effect the reduction of numerous metallic oxides without the employment of carbon, and to produce numerous useful and important alloys.

ACTION OF THE HALOID ACIDS, IN GAS FORM UPON MOLYBDIC ACID.

BY EDGAR F. SMITH AND VICKERS OBERHOLTZER.

[*Read before the Chemical Section, April 18, 1893.*]

Debray (*Comp. rend.*, xlvi, 1098, and *Annalen der Chemie und Pharmacie*, **108**, 250), first called attention to the fact that a very volatile, crystalline compound of the formula $MoO_3 \cdot 2HCl$ resulted upon exposing molybdic acid, heated from 150–200° C., to the action of hydrochloric acid gas. It is true that the constitution of this volatile product may also be represented by the formula $MoO(OH)_2Cl_2$, which would make it a molybdenum hydroxychloride. Dismissing the question of constitution for the present, and considering the point of ready volatility, it seemed to us that this behavior might be utilized for the separation of molybdic acid from tungstic acid, as the latter apparently does not enter into volatile combination with hydrochloric acid gas. We, therefore, exposed weighed amounts of sublimed molybdic acid to the action of the acid gas and succeeded in expelling the molybdic acid completely from the porcelain boats containing it. Applying the same treatment to what we considered pure tungstic acid, we were greatly surprised to discover that very appreciable quantities of a sublimate, similar in every respect to that of molybdenum hydroxychloride were expelled from the boat. An examination of this product proved it to be the molybdic acid compound. In short, our tungstic acid was not pure. We, however, continued to heat portions of it in hydrochloric acid gas until a sublimate was no longer formed, when on mixing molybdic acid in known amount with the residual tungstic acid, we discovered that we could completely expel the former acid from the latter. Our next step was to observe the effect of heating anhydrous sodium molybdate in hydrochloric acid gas. The appended results show a quantitative conversion into sodium chloride, consequently a complete volatilization of the molybdic acid:

Na_2MoO_4 in Grams.	$NaCl$.	$NaCl$ Required.
0·1302 gave at 150–200°,	0·0738	0·0739
0·1832,	0·1038	0·1040
0·2046,	0·1159	0·1162
0·3845,	0·2186	0·2183

As we were about to apply this method to the quantitative separation of molybdic and tungstic acids, both present as sodium salts, a closer scrutiny of the existing literature relating to this subject revealed that E. Péchard (*Compt. rend.*, **114,** 173, and *Zeit. f. anorg. Chemie*, **1,** 162) had already carried out the determination of molybdic acid and its separation from tungstic acid in this way with very evident success. Our own experiments confirm those of Péchard in every particular.

As previously observed, the tungstic acid that we thought pure contained molybdic acid. Traube (*Neues Jahrbuch für Mineralogie, Geologie und Paläontologie, Beilageband*, **7,** 232) has demonstrated that natural calcium tungstate, scheelite, and commercial tungstic acid obtained from the mineral wolframite, contain molybdic acid. E. Corleis (*Liebig's Annalen*, **232,** 265), has shown that the latter acid is even present in the "Wolframsaeure puriss" of trade, while Friedheim (*Zeit. f. anorg. Chemie*, **1,** p. 76) asserts that commercial sodium tungstate is strongly contaminated with sodium molybdate, and that even when exercising the greatest care in the process of purification the tungstate continued to show traces of molybdenum.

We found molybdic acid present in the purest sodium tungstate that we could get, and in the minerals scheelite and wolframite, when these were exposed to the action of hydrochloric acid gas at a temperature not exceeding 400° C. Hence, we are disposed to regard this method as excellently adapted for the detection of molybdic acid, as well as for the purification of tungstic acid and tungstates containing molybdenum.

Our original purpose having been the study of the behavior of molybdic acid in atmospheres of all the gaseous haloid acids, we may now briefly recount our experiences in those directions.

Action of Hydrobromic Acid, in Gas Form, upon Molybdic Acid. —The molybdic acid used by us was purified by converting the commercial acid into the ammonium salt, which was recrystallized a number of times and then ignited with air access. The product was sublimed very carefully from a platinum crucible. The hydrobromic acid was prepared by dropping bromine from a separatory funnel upon crude anthracene contained in a half-litre flask. It passed through a hard-glass tube, six inches in length, filled with anthracene, then through two U-tubes containing a paste of amorphous phosphorus, and two U-tubes provided with fused calcium chloride, while the sixth and last tube contained phosphoric anhydride. Having completed this circuit it was admitted to a perfectly dry combustion tube, into which had been introduced a porcelain boat filled with molybdic acid. The anterior portion of the combustion tube was closed with a calcium chloride tube to exclude all moisture. The heat used in the experiment was supplied from a combustion furnace. An ordinary thermometer was placed above the combustion tube; its bulb rested directly over the boat. In this manner we recorded the approximate temperature at which the reaction took place. As soon as the entire apparatus was filled with the gas, three burners of the furnace, directly under the boat, were lighted, and the heat gradually raised until it reached 200° C. A change took place almost instantly. Just beyond the boat appeared a heavy sublimate, with a color resembling that of potassium permanganate. Beyond this solid a brownish yellow colored liquid separated; on cooling it changed to long, beautiful yellow needles. These proved to be unstable, melting almost immediately when brought in contact with the air. At the expiration of an hour the passage of the hydrobromic acid gas was interrupted. The permanganate colored sublimate was removed from the sides of the tube as completely as possible, introduced into a porcelain boat and then carefully resublimed in a current of dry carbon dioxide. The compound sublimed in fern-like aggregates, consisting of dark red or purple red, shining, overlapping plates, extending from one side of the combustion tube to the other. They dissolved in water with liberation of heat. Their aqueous solution was colorless, but upon standing became blue in color. The crystals themselves changed in appearance on prolonged exposure to the air. By preserving them in an atmosphere of carbon dioxide they suffered no decomposition. Examined under a polarization microscope they showed their ability to polarize light, and that they consisted of aggregations of perfectly square plates. After the re-sublimation portions of the substance were weighed off in weighing tubes and analyzed. For the bromine determination the material was dissolved in as little cold water as possible, dilute nitric acid added, and this followed immediately with silver nitrate. The resulting silver bromide was treated in the usual manner. In estimating the molybdenum, the substance was brought into a weighed porcelain crucible and dilute nitric acid added. The solution was evaporated almost to dryness at a very gentle heat, when the crucible contents were treated with concentrated nitric acid, after which followed evaporation to perfect dryness. This operation was repeated and a gentle but direct heat applied to the crucible for periods varying from one-half to one hour. This was done to fully oxidize the molybdenum to trioxide. Portions of the new compound were mixed with freshly ignited litharge and heated in a current of dry air, using a perfectly dry combustion tube, provided with a weighed calcium chloride tube. The weight of the latter showed no increase, so that we were safe in considering our substance free from hydrogen.

ANALYSES.

Bromine Determination.

	Ag. Br.		*Bromine percentage.*
0·1334 grams substance gave	0·1793 gr.	=	57·19
0·3353	0·4499 "	=	57·09
0·0680	0·0908 "	=	56·82

The mean of these bromine percentages is 57·037 per cent.

Molybdenum Determination.

		MoO_3.		*Molybdenum percentage.*
0·2545 grams substance gave	. . . .	0·12865 gr.	=	33·69
0·2916	. . . .	0·1466 "	=	33·52
0·1115	. . . .	0·0559 "	=	33·42

The mean of the molybdenum percentages is 33·54 per cent.

We experienced difficulty in wholly eliminating the traces of blue oxide in all of the molybdenum determinations, hence we look upon the results given above as low.

Regarding our compound as consisting of molybdenum, bromine and oxygen with the above percentages, and taking the oxygen by difference, we deduce as the most probable formula $MoO_2Br_2,MoOBr_2$ or $Mo_2O_3Br_4$—molybdenum sesquioxide tetrabromide. The theoretical requirements of this formula are: 34·28 per cent. Mo, 57·19 per cent. Br. and 8·57 per cent. O.

The only existing molybdenum oxybromide until the present has been MoO_2Br_2—molybdenyl bromide, discovered by Blomstrand on passing bromine vapor over the heated dioxide of molybdenum, or by heating a mixture of molybdic acid and boron trioxide with potassium bromide. It is mentioned as forming yellow, deliquescent tablets. For the sake of comparison, we made Blomstrand's compound by the second method. We found that when it was sublimed upon a previously heated portion of the tube it separated in "*mehr ausgebildeten Krystalltafeln auf; bei rascher Sublimirung in undeutlich krystallinischen Schuppen. Farbe schön gelbroth*" (Blomstrand, *Jour. prk. Chemie*, **82**, 439). Our compound, however, is formed simultaneously with that of Blomstrand when vapors of bromine are conducted over heated molybdic acid; the tube in which this reaction was made was freed from air by conducting bromine vapors through it and heat was not applied until we were satisfied that bromine alone was present.

The brownish-yellow liquid formed at the same time with the purple-red colored solid was crystallized in the tube in which it had been produced; the tube was then severed at a point between the yellow and red-colored compounds. The yellow immediately liquefied on exposure to the air. The liquid was collected in a small and previously weighed beaker; this was then placed in a sulphuric acid desiccator and the air exhausted. At the expiration of from two to three days the yellow needles had re-formed. The beaker and its contents were then rapidly weighed. Water was poured on the needles; their solution was colorless or slightly yellow tinged. On standing, the liquid slowly acquired a deeper yellow or reddish-yellow hue, and after twenty-four hours a blue oxide of molybdenum had separated.

The bromine and molybdenum of this product were determined in the same manner as in the purple-colored solid. We, however, had no difficulty in obtaining perfectly white molybdic acid in all the determinations that follow:

ANALYSES.

Bromine Determination.

	Silver Bromide.		*Bromine percentage.*
0·0950 grams substance gave	0·1403 gr.	=	62·83
0·2523	0·3700 "	=	62·50
0·2709	0·3967 "	=	62·37
0·0250	0·0365 "	=	62·12

The mean percentage equals 62·45 per cent.

Molybdenum Determination.

	MoO_3.		*Percentage of Mo.*
0·0946 grams substance gave	·0346 gr.	=	24·39
0·0946	·0337 "	=	23·75
0·1892	·0686 "	=	24·06

The mean of these percentages is 24·03 per cent. The formula we deduce from these results is $MoO_3 \cdot 3HBr$; it perhaps might be better represented as a trihydroxybromide $MoO(OH)_3Br_3$. The theoretical requirements are 62·02 per cent. Br and 24·80 per cent. Mo.

It is interesting to note that the long, yellow-colored needles of this compound were also obtained upon passing hydrobromic acid gas over the oxybromide of Blomstrand at a gentle heat. This change may easily be conceived as occurring if we grant the presence or production of water through the formation of secondary products.

$$MoO_2Br_2 + H_2O + HBr = MoO_3{\cdot}3HBr.$$

As we were not in a position to ascertain the true composition of the individual substance or substances from scarcity of material, we offer the above suggestion as a possible explanation for the appearance of the hydroxybromide in the manner just indicated.

Action of Hydriodic Acid, in Gas Form, upon Molybdic Acid.—A violent reaction occurred, in the cold upon passing the dry acid gas over molybdic acid; much heat was evolved, and iodine was liberated. The non-volatile product that remained in the boat possessed a bright violet color. It was exposed for a period of two hours to a temperature ranging from 45–50° C., during which time a continuous stream of dry and pure gas was conducted over it. Carbon dioxide was next introduced and passed for an equal period, while the temperature was maintained at 50° C. The results obtained from many analyses of this product pointed to the probable composition MoO_3HI, but as the quantity of iodine varied according to the length of time during which the hydriodic acid gas acted and with the temperature, we feel unable to assign any definite composition to the compound. It has seemed to us, from a careful study of the experimental results, that several derivatives were formed, but we were unable to separate them, and indeed by continuing the action of the gas for periods varying from six to eight hours, at the same time elevating the temperature from 105 to 120° C., iodine continued to separate. At last a violet-blue colored product remained; this appeared to be homogeneous. Prolonged action of the gas was without further reduction, therefore carbon dioxide was introduced to expel it. The blue colored product suffered no change on exposure to the air. We obtained what appeared to be the same substance by exposing the iodine-containing compound mentioned above to a temperature of 200° C., in an atmosphere of carbon dioxide. Indeed, mere exposure of the iodine compound to the air for some time gave the blue-colored derivative.

The same form of apparatus was used here that we have described with the oxybromides. The hydriodic acid gas was made from moist phosphorus and iodine. It was carefully dried.

Analyses.—An analysis of the blue-colored residue resulted as follows: The molybdenum was determined as under the bromine derivatives:

	Mo_3O.		*Mo* *Per Cent.*
0·1099 grams substance gave	0·1053 gr.	=	64·19
0·1017	0 0972 "	=	63·72
0·0807	0·0775 "	=	64·02
0·0959	0·0937 "	=	64·92
0·1386	0·1350 "	=	64·93

The mean molybdenum percentage is therefore 64·35 per cent.

Water Determination.

	H_2O		*Per Cent.*
0·1533 grams substance gave	0138 gr.	=	9·00
0·1673	·0142 "	=	8 49

The mean of these percentages would therefore be 8·74 per cent. An intense red heat was required to fully expel this water content. The figures obtained would lead to an oxide of the formula $Mo_4O_{10},3H_2O$; this would require 64·21 per cent. Mo and 9·03 per cent. H_2O. Iodine was not found in the compound. The dehydrated residue was brown in color. Three determinations of its molybdenum content indicated it to be Mo_2O_5. As a result then of the action of hydriodic acid gas upon molybdic acid we can point to no definitely iodated product, but to a blue oxide, a product of reduction. In this connection we may direct attention to the observation of Schulze (*Journ. prk. Ch.* (N. F.), **29**, 440) that molybdic acid sustains reduction when heated with potassium iodide, air being excluded. The resulting products possess variable composition, but by the use of four parts of molybdic acid and one part of potassium iodide a definite product was prepared. It proved to be a new oxide of molybdenum, steel blue in color, crystalline and possessing metallic lustre. Its analysis gave results agreeing with the formula Mo_4O_{11}. Our reduction product is quite analogous to this, except that it is hydrous.

Action of Hydrofluoric Acid, in Gas Form, upon Molybdic Acid.—The hydrofluoric acid gas was evolved from fluorspar and sulphuric acid. It passed directly over the molybdic acid contained in a platinum boat and the latter in a platinum combustion tube from which a delivery tube led into a platinum flask, cooled by ice water. At a temperature ranging from 300–400° C., all the molybdic acid was converted into a volatile product that collected upon the anterior portions of the platinum combustion tube in crystals, having a peculiar red color. On holding the tube in which these crystals had been sublimed toward the light, it appeared to be filled with violet vapors of iodine; this was, however, due to reflection of light from the sides of the flat needle-like crystals. It is scarcely necessary to remark that before disconnecting the apparatus, carbon dioxide was conducted through it to expel the hydrofluoric acid. The platinum flask also contained the volatile molybdenum product. Much hydrofluoric acid was with it. This was expelled by the introduction of the carbon dioxide.

The new product when removed from the vessels containing it was found to be deliquescent, and it gradually decomposed into a blue oxide of molybdenum. It attacked glass, was insoluble or nearly insoluble in water, but dissolved to a colorless liquid in hydrofluoric acid. Portions of it were weighed off as rapidly as possible in platinum crucibles, and the molybdenum determined as trioxide by evaporation with nitric acid, followed by gentle ignition.

Molybdenum Determination.

	MoO_3.		Mo. Per Cent.
0·0526 grams substance gave,	0·0479 gr.	=	60·70
0·1066	0·0967 "	=	60·66
0·1166	0·1051 "	=	60·94
0·1265	0·1164 "	=	61·35

The mean of these determinations is 60·91 per cent. Mo. Formed in the same manner as molybdenum sesquioxide tetrabromide, we find that these results agree very closely with an oxyfluoride of analogous formula $Mo_2O_3Fl_4$, which would require 60·76 per cent. Mo. In experimenting with the above oxyfluoride we several times observed a slight quantity of a colorless liquid, which upon careful evaporation with nitric acid left a very appreciable quantity of molybdic acid. It may, perhaps, be an analogue of the very volatile $MoO_3 \cdot 2HCl$, and the unstable, liquid $MoO_3 \cdot 3HBr$. We endeavored to fix its composition, but experienced so great difficulty in getting material that we could safely consider sufficiently pure that we abandoned it entirely. The work attending its preparation is anything but pleasant and the yield exceedingly uncertain.

But one other oxyfluoride of molybdenum is known; namely, that prepared by Schulze (*Jour. prk. Chemie* (N. F.), **21**, 442), by fusing metallic fluorides together with molybdic acid with the exclusion of air. It has the constitution represented by the formula MoO_2Fl_2.

Reviewing the action of the gaseous haloid acids upon molybdic acid we observe:

(1) That hydrochloric acid gas converts the acid into a solid, very volatile product $MoO_3 \cdot 2HCl$.

(2) That hydrobromic acid changes molybdic acid to a volatile brownish-yellow liquid, $MoO_3 \cdot 3HBr$, forming long yellow needles at low temperatures and under diminished pressure, as well as a beautifully crystallized solid of the formula $Mo_2O_3Br_4$.

(3) That hydriodic acid reduces molybdic acid to a new oxide $Mo_4O_{10} \cdot 3H_2O$.

(4) That hydrofluoric acid converts the molybdic acid into at least one well-formed but volatile product, having the constitution represented by the formula $Mo_2O_3Fl_4$.

Püttbach (*Annalen*, **201**, 137) divides the known molybdenum oxychlorides into two classes:

Saturated.	*Unsaturated.*
$MoOCl_4$	$Mo_3O_3Cl_7$
$Mo_2O_3Cl_6$	
$Mo_3O_5Cl_8$	$Mo_2O_3Cl_4$
MoO_2Cl_2	

But one oxybromide is known. Its formula is MoO_2Br_2. Our experiments add to this, the compound $Mo_2O_3Br_4$, which would correspond to $Mo_2O_3Cl_4$. The latter is light brown in color, while the former possesses a deep purple color. Schulze's oxyfluoride would correspond to MoO_2Cl_2 and MoO_2Br_2, while that obtained by us corresponds to $Mo_2O_3Cl_4$ and $Mo_2O_3Br_4$. Püttbach's division presupposes the presence of a sexivalent molybdenum atom in the saturated members, while the unsaturated are regarded as derived from two molecules of $MoCl_5$ by the substitution of oxygen for equivalent amounts of chlorine. Our oxybromide, $Mo_2O_3Br_4$, and oxyfluoride, $Mo_2O_3Fl_4$, may be looked upon as possessing similar origin, although their corresponding pentabromide and pentafluoride are unknown. The compound $MoO_3 \cdot 3HBr$, like $MoO_3 2HCl$, presupposes the presence of a sexivalent molybdenum atom and may be properly considered a hydroxybromide, represented by the formula $Mo(OH)_3Br_3$, a derivative of the unknown hexabromide $MoBr_6$.

CHEMICAL LABORATORY OF THE
UNIVERSITY OF PENNSYLVANIA, APRIL 15, 1893.

[*Proceedings of the special meeting held Thursday, June 8, 1893.*]

HALL OF THE FRANKLIN INSTITUTE,
PHILADELPHIA, June 8, 1893.

Dr. WM. H. GREENE, President, in the chair.

The object of this meeting was to afford the members the opportunity of hearing a lecture by Dr. Ernest Milliau, Director of the Government Testing Laboratory at Marseilles, France, on "The Methods of Testing Fats and Oils."

The lecture was delivered for the purpose of furthering the adoption of uniform methods of testing and of expressing results.

A vote of thanks to the lecturer was carried, and it was voted also to refer the lecture for publication in the *Journal* as part of the proceedings of the Section.

Adjourned. WM. C. DAY, *Secretary.*

[*Proceedings of the stated meeting, held Tuesday, June 20, 1893.*]

HALL OF THE FRANKLIN INSTITUTE,
PHILADELPHIA, June 20, 1893

Dr. WM. H. GREENE, President, in the chair.

Letters from Prof. E. F. Smith and Mr. Lee K. Frankel were read, expressing regret at their inability to be present at the meeting.

The President announced the death of Mr. C. J. Semper. Dr. Terne spoke of the work and character of the deceased, and the President appointed Dr. Terne and Dr. Wahl members of a committee to prepare a memorial; he also gave them authority to appoint a third member.

The proceedings of the special meeting of the Section, held June 8th inst., were ratified by a unanimous vote.

Dr. Terne then read a highly interesting paper on "The Rational Utilization of City Garbage." This paper was very opportune, in view of the steps now being taken in Philadelphia to cremate and thus totally destroy garbage for sanitary reasons. Dr. Terne advocated the adoption of a system by which a saving of the valuable oil and fat ingredients of garbage could be effected, while the residue from this could be utilized as a valuable fertilizer. The members of the Section were unanimous in indorsing the view of Dr. Terne that garbage could be so utilized with a saving of much valuable material which is ordinarily wasted, and under the system of cremation totally destroyed. They also agreed that the ends of sanitarians would be just as effectively secured by the proposed system as by the wasteful process of cremation. The author further described some of the details of treating the garbage for the purpose he advocated, and exhibited samples of products, such as oils, solid fats and fertilizing material, which he had already secured on the large scale.

The Secretary then read a paper by Mr. Lee K. Frankel on "Gelatinous Silver Cyanide," and also exhibited a specimen of the compound submitted by the author.

The Section then adjourned. WM. C. DAY, *Secretary*.

THE ACTION OF AMMONIA GAS UPON MOLYBDENYL CHLORIDE.

BY EDGAR F SMITH AND VICTOR LENHER.

[*Read before the Chemical Section, May 16, 1893.*]

In 1857, Tuttle (*Annalen*, **101**, 285) studied the action of ammonia upon molybdenum trioxide, and molybdenum chloride ($MoCl_4$). In the case of the trioxide the temperature at which the reaction was made approached a red heat. The resulting product was in part black in color and possessed metallic lustre. Its analysis revealed the presence of nitrogen, oxygen, hydrogen and molybdenum. The quantity of the latter constituent equalled 92·9 per cent. Upon conductivity the reaction at more elevated temperatures, the product was found to contain 77·9 per cent. and 73 per cent. of molybdenum, while the hydrogen content did not exceed 0·18 per cent. The results consequently were not constant.

On exposing molybdenum chloride to the action of ammonia gas at a temperature just sufficient to volatilize the ammonium chloride which arose in the reaction, Tuttle obtained a black, metallic sintered mass. It was found to contain 82·83 per cent. of molybdenum and was assumed to have the composition expressed by the formula $Mo_2N_2 + Mo(NH_2)_2$, analogous to a compound of tungsten obtained in a similar manner by Wöhler (*Annalen*, **73**, 190).

Several years after the publication of the preceding investigation, Uhrlaub presented an inaugural thesis, entitled "Die Verbindungen einiger Metalle mit Stickstoff" (Goettingen, 1859), from which we collate the following interesting facts: In the action of ammonia gas in the cold upon molybdenum chloride much heat was evolved and a black colored product resulted; its analysis showed the presence of 76·457 per cent. of molybdenum, 23·134 per cent. of nitrogen and 0·677 per cent. of hydrogen. In subsequent experiments

Uhrlaub employed a more intense heat, thus hoping to eliminate the slightest hydrogen content, but this element continued to show itself in his various products, until on raising the tube in which the reaction took place to an intense red heat he obtained a compound that careful analysis gave a composition which may be expressed by the formula Mo_3N_2. In other words, a molybdenum nitride had been formed by acting upon the chloride of the metal with ammonia gas at a high temperature.

When Uhrlaub tried the action of ammonia upon molybdic acid at a gentle heat, he obtained "pseudomorphuen," as he designated them, bluish-black in color. Several were prepared; they varied much in composition. Uhrlaub attributes this variation to the different degrees of heat employed and to the length of time during which the heated molybdenum trioxide was exposed to the action of the gas.

The preceding facts indicate that the action of ammonia gas, either upon the trioxide or chloride, is not as simple as might be presumed. An amide that might well be expected in either case appears not to have been obtained by either Tuttle or Uhrlaub.*

We hope to reach this result by the action of ammonia gas upon molybdenyl chloride, in accordance with the equation

$$MoO_2Cl_2 + 4NH_3 = MoO_2(NH_2)_2 + 2NH_4Cl.$$

It will be noticed that we apply the term molybdenyl chloride to the compound generally called molybdenum dioxychloride. Our assumption of molybdenyl is based upon the terms sulphuryl, chromyl, etc., applied to compounds possessing a constitution similar to that of the dioxychloride of molybdenum MoO_2Cl_2, SO_2Cl_2, CrO_2Cl_2.

Preparation of Molybdenyl Chloride.—Of the various methods proposed for the formation of this derivative of molybdenum we discovered that the action of dry chlorine upon the dioxide of the metal yielded by far the most satisfactory product, both as to purity and quantity. At a very gentle heat the molybdenyl chloride forms rapidly and sublimes in feathery crystals. Schulze (*Jr. Prakt. Chemie*, **29** (N. F.), p. 440), in discussing the action of molybdic acid upon metallic chlorides, proposes this procedure for the object we had in view, but we failed to meet with success in our application of the method. The yield was not very abundant.

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* The primary object of these gentlemen seems to have been the preparation of molybdenum nitrides.

The crystalline molybdenyl chloride, prepared as described, was introduced into porcelain boats, and these placed in tubes of hard glass, through which we conducted a brisk current of well-dried ammonia gas. The molybdenyl chloride immediately assumed a deep-black color, much heat was evolved and copious fumes of ammonium chloride vapor were carried out of the tube. Considerable moisture also collected upon the anterior portion of the combustion tube. At last heat sufficient to expel any ammonium chloride retained by the compound was applied; but it was not for a longer period than half an hour. The boat and contents were cooled in ammonia gas. The product of the reaction was placed over sulphuric acid to absorb any retained gas; a portion of it was also washed with water, and the aqueous solution examined for chlorine, but this was not found present. In general appearance the product was metallic and black in color. Analyses were made of different preparations. The molybdenum content was determined by oxidizing weighed portions of material with dilute nitric acid, evaporating carefully to dryness, finally applying a gentle heat for a period of fifteen minutes.

The hydrogen was estimated by burning the material in a current of oxygen, and collecting the water that was produced in a weighed calcium chloride tube.

The nitrogen estimations were three in number; one of them was carried out by the method of Dumas, while the other two were made by the soda-lime process.

The oxygen was obtained by difference.

Our analytical results may be tabulated as follows :

Molybdenum Determination.

	MoO_3 found.		Mo Per Cent.
(1) 0·1047 gram substance taken, ...	0·1156 gr.	=	73·65
(2) 0·1006	0·1108 "	=	73·42
(3) 0·1004	0·1110 "	=	73·70
(4) 0·1028	0·1113 "	=	73·47
(5) 0·1017	0·1126 "	=	73·80

The mean molybdenum percentage of these five determinations is 73·61 per cent.

Hydrogen Determination.

	Water found.		H Per Cent.
0·2088 gram substance taken, ...	·0082 gr.	=	0·43

Nitrogen Determination.

	Pt. found.		N Per Cent.
(1) 0·1510 gram substance taken, ...	·0643 gr.	=	6·05
(2) 0·1529	·0642 "	=	5·96

The nitrogen found by the Dumas method equalled 6·00 per cent. and the mean of the three nitrogen estimations was also 6·00 per cent.

Two-thirds of this nitrogen content were expelled when our compound was exposed to the action of hydrogen at the highest temperature attainable with a good combustion furnace.

Taking the mean of our analyses as a basis of calculation :

	Per Cent.
Mo, ...	73·60
N, ...	6·00
H, ...	0·43
O (by difference), ...	19·96

we deduce $Mo_5O_8N_3H_3$ as the most probable empirical formula, which may be variously written to express the enigmatical constitution of this compound. Thus it might be $MoO(NH)_2$. MoONH. $3MoO_2$, or 4 MoO_2. $Mo(NH)_3$, which may be correctly termed tetramolybdenyl molylbdenimide.

Our compound is stable in the air. Hydrochloric acid does not affect it. Nitric acid of sp. gr. 1·42 causes it to burn very energetically. Dilute alkalies attack it very sluggishly. It liberates ammonia when fused with caustic potash. When heated in a current of oxygen it is slowly oxidized. Heated in nitrogen gas the black compound loses water and assumes a reddish color. An analysis of this product indicates that it was probably molybdenum dioxide mixed with a very small amount of nitride; at least, traces of nitrogen were found upon examination. Another interesting observation was that when the black product was introduced into an aqueous solution of silver nitrate, crystals of metallic silver gradually appeared over the surface of the molybdenum compound.

We obtained our first product several times, but care must be exercised and the same conditions noted by us strictly observed if success in its formation is desired.

An examination of Uhrlaub's analytical results will show that one of his products approaches very closely the compound we have just described. He speaks of it as a black "pseudomorph" with the composition:

	Per Cent.
Mo,	73·55
N,	5·58
H,	0·54
O,	20·30

The formula deduced from these figures differs from that presented by us, and what is more, if we understand Uhrlaub correctly, his compounds, prepared from ammonia gas and molybdenum trioxide, were all "blau-schwarz" in color, and were not acted upon in the cold by nitric acid (see his dissertation, pp. 13, 14, 17).

However, it is evident that the product we obtained by the action of ammonia gas upon molybdenyl chloride is not the amide we had in view. Thinking that perhaps the heat we applied to drive out the final traces of occluded ammonium chloride may have been sufficient to alter the composition of the product formed at first, we allowed the ammonia to act upon the molybdenyl chloride at the ordinary temperature, and when there was no further evolution of ammonium chloride and the boat had become perfectly cold* we introduced carbon dioxide, applying a very gentle heat at the same time, but we failed to achieve our aim. Nitrogen when substituted for carbon dioxide gave us no better result. We next dissolved molybdenyl chloride in the purest ether we could get and conducted ammonia gas into this solution. We obtained decomposition products. A closer examination of the behavior of the molybdenyl chloride towards ether revealed the fact that the moment the two came in contact a slight hissing sound was perceptible and the ether at once imparted a strong acid reaction to blue litmus. The same was observed when pure chloroform was employed as a solvent.

If molybdenyl chloride be gradually heated in an ammonia atmosphere until the tube of hard glass becomes bright red in color and the gas action be continued for the period of an hour, the resulting product will be an amorphous, metallic, black mass. Subjected to analysis it gave results as appended:

Molybdenum Determination.

	MoO_3 found.		*Mo. Per Cent.*
(1) 0·1042 gram substance taken, . . .	0·1061 gr.	=	67·87

Nitrogen Determination.

0·1025 gram substance burned with soda lime gave 7·00 per cent. N.

Hydrogen Determination.

0·1012 substance ignited in a current of oxygen gave ·0109 gram of water equal to 1·19 per cent. H.

	Per Cent.
Mo,	67·87
N,	7·00
H,	1·19
O (by difference),	23·94

The empirical formula deduced from these figures is $Mo_7O_{14}N_5H_{10}$, which can also be written

$$4MoO_2.2MoO_2(NH_2)_2.MoO_2NH_2$$

Dilute alkalies have no effect upon this compound; but it liberates ammonia when fused with caustic potash. It is converted into molybdenum trioxide very energetically—with evolution of sparks—when brought in contact with cold nitric acid.

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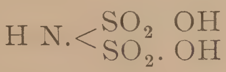
* Portions of the product removed at this stage and shaken with cold water decomposed into a mixture of blue- and brown-colored masses. The possibility of removing the ammonium chloride was, therefore, excluded.

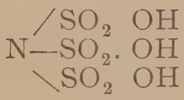
Other products were obtained by us; their analyses lead us to the conclusion that with us as with Uhrlaub the composition of the derivative depended wholly upon the length of time during which the gas acted upon the molybdenyl chloride, and the degree of heat employed in the experiment. It seems highly improbable to us that the amide $MoO_2(NH_2)_2$—molybdenyl amide—can be prepared after the fashion pursued by us, for it is quite certain that the heat of the reaction evolved in the first contact of the ammonia with the molybdenyl chloride exercises a very potent influence upon the composition of the product.

When we recall the action of ammonia gas upon sulphur trioxide and sulphuryl hydroxy-chloride resulting in the compounds with the following constitution :

$$H_2N.SO_2\ OH$$



$$H\,N.<\begin{matrix} SO_2\ OH \\ SO_2.\,OH \end{matrix}$$



The question that obtrudes itself is: Are not these products and their methods of formation types of the processes and results that have occurred not only in our studies described in this paper, but also in the studies of Tuttle and Uhrlaub?* Are not their products as well as our own only residues of amide, imido, and nitrito molybdic acids?

Above we have written for our first product the constitutional formulæ $MoO(NH)_2$. $MoONH.3MoO_2$, and $4MoO_2.Mo(NH)_3$, but after considering the sulphur types we would express our empirical formula $Mo_5O_8N_3H_3$ differently, as follows:

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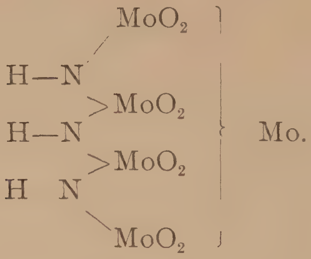
* At least in so far as the action of ammonia gas upon molybdenum trioxide was concerned.



We have here several broken-down molybdenyl amide nuclei in conjunction, not chemically combined, with metallic molybdenum. Reviewing the behavior of the product which we thus graphically represent, we may be allowed to emphasize the fact that when it was brought in contact with an aqueous argentic nitrate solution metallic silver was precipitated, and this we know from Smith's* observation is a property of metallic molybdenum. Further, it will be recalled that when our product was heated in an atmosphere of nitrogen it left a reddish-colored compound, which upon analysis approximated the requirements of molybdenum dioxide, and that traces of nitrogen were also detected in it. All these experimental facts find expression in our graphic representation above.

The second product obtained by us was even more active when introduced into a silver nitrate solution, throwing out metal quite rapidly, proving in our opinion the presence in it of even a greater quantity of metallic molybdenum than is contained in the first body. Similar reduced molybdenyl amide nuclei mixed with metallic molybdenum, could also be constructed for our second compound, and be in harmony with the observed deportment of this body if it were necessary.

University of Pennsylvania,
Philadelphia, May 16, 1893.

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* *Zeitschrift für anorg. Chemie*, **1**, 360.

GELATINOUS SILVER CYANIDE.

By Lee K. Frankel

[*Read before the Chemical Section, June 20, 1893.*]

In the *Comptes Rendus*, **73**, 998, Stas has described the occurrence of four different varieties of silver chloride, viz:

(*a*) the gelatinous;
(*b*) the cheesy, flocculent;
(*c*) the pulverulent;
(*d*) the granular crystalline variety.

No methods are given for obtaining these varieties, nor could the author find any reference in the literature to any other salts of silver having the above properties. The following will, therefore, be of interest.

Recently the author instructed one of the students in the University laboratory to reduce silver chloride to metallic silver by fusion with potassium cyanide. As the work was purely experimental, no weighed quantities of the substances were taken, nor was any notice taken of the temperature at which the fusion took place. The cooled mass and porcelain crucible were placed in a beaker, covered with water, boiled for thirty minutes, and then put aside until the following day. On examining the contents of the beaker, instead of finding the liquid above the crucible clear, as had been expected, it was filled with a transparent gelatinous mass, somewhat resembling aluminum hydrate, but of greater consistency. A portion of this precipitate was removed from the solution, carefully washed with cold water until the filtrate reacted neither with silver nitrate nor with dilute hydrochloric acid, and then carefully dried.

A qualitative examination showed the following: The substance is readily soluble in ammonium hydroxide, from which solution it is re-precipitated by nitric acid. It does not fuse on heating, but decomposes readily, leaving a residue of metallic silver. The presence of cyanogen was readily detected by the "prussian blue" reaction. No chlorine was found.

A quantitative estimation of the silver in the substance gave a result which was five per cent. lower than the theoretical amount of silver in silver cyanide.

This is in all probability due to the impurities contained in the compound, which arise from the potassium cyanide used in its preparation.

The amount of substance used in the analysis was very small, since what appeared to be a rather large quantity of the original, moist, gelatinous compound, shrivelled to a very small bulk on drying.

Repeated attempts have since been made to procure more of the substance for analysis, but all efforts have so far been futile. The amounts of silver chloride and potassium cyanide used have been varied, and the fusion likewise has been made at different temperatures, but without success. It is the intention of the author to fuse silver cyanide with potassium cyanide, and thereby to obtain the desired result.

UNIVERSITY OF PENNSYLVANIA,
PHILADELPHIA, June 15, 1893.

THE UTILIZATION OF GARBAGE.

BY DR. BRUNO TERNE.

[*A paper read at the meeting of the Chemical Section, held June 20, 1893.*]

The immortal Justus Liebig, the founder of agricultural chemistry, and, indirectly, by his teachings, the creator of the industry of artificial fertilizers, combined in himself the qualifications of a most eminent chemist and a far-sighted national economist.

He transformed the chemical doctrines of plant nutrition at once to available figures for the farmer to show him in clear and indubitable sentences the laws of nature which compel him to restore to the soil what he has taken from it in the form of the products of the field.

His classical *Chemical Letters* are a monument he has erected for himself which will endure as long as the conditions of this globe remain the same as they now are. As long as the human race lives, the fundamental laws requiring the restitution to the soil in available form of the constituents of the plants as laid down by Germany's most eminent agricultural chemist will be written in golden letters in the history of all civilized nations.

In centuries to come the classical works of Liebig will be revered as the revelation of science respecting the practice of agriculture.

In his forty-seventh letter, Liebig refers especially to the relation of the consumption of the great cities to the products of our farms. From each hectare of wheatfield, the farmer, from the return of an average harvest transports from his farm to the consumers, 4,000 pounds of grain containing seventy pounds of mineral substances, mainly phosphoric acid and potash.

The refuse of a city of 1,000,000 inhabitants will amount, in dried form, per annum, to 45,000,000 pounds.

The constituents of this powdered material are 10,300,000 pounds of mineral substances, mostly the mineral parts of breadstuffs and meat, which contain no less than 4,580,000 of phosphatic salts.

The removal of this precious material (at the rate above-named) from the fields has been going on for centuries and only a small portion of it finds its way back to the fields.

It is folly to think that the loss of this material has had no detrimental influence upon the fertility of the soil.

I will quote from the tenth letter of Henry C. Carey, the American statesman and national economist, to the President of the United States. [J. B. Lippincott, Phila., 1858.]

"The national economical question is not how much we can produce but how much is returned to the soil of the products annually.

"Labor used to rob the soil is worse than labor thrown away. In the latter it is a loss to the present generation, in the former poverty for the coming generation."

The same system which Carey condemned, in the above citation, of a large export of material without corresponding restitution of plant food to the soil continues to be practised in the corn belt of the West, while the cotton belt of the South and the entire East have been compelled to yield to the inexorable law of nature, and must now restore food to the impoverished soil to raise their crops.

The zone subservient to artificial nutrification of the soil grows wider and wider from year to year, since the waste of plant food-material grows more serious as our population grows denser.

What Carey so incisively pointed out thirty-five years ago, is as true to-day as it was then, but only the stress of absolute necessity, or the prospect of financial gain, will suffice to alter the system involving the extravagant waste of plant food-material which is now the rule with us.

For the sake of convenience we pollute our rivers and choose rather to suffer the consequences of drinking polluted water than to adopt rational measures to save, for the enrichment of our fields, the products which the law of nature has provided for the very purpose.

Our antipodeans, the much-despised Chinese, are much better practical economists than their civilized brethren.

In China, nothing is allowed to go to waste that is useful to the soil. The Chinaman's house is without the improved devices of the modern plumber, and his scent for nuisances may not be so highly cultivated as ours, but by his system of the strictest economy, he manages to keep up the fertility of his soil to so high a degree, that the vast empire, notwithstanding that it possesses the densest population on the face of the earth, is entirely independent of all other nations, not only for the breadstuffs and other food supplies required for the sustenance of its people, but also for the fertilizing materials needed for its soil.

The Chinese, with the instinct of self-preservation, have been doing for centuries what Liebig and his followers taught the civilized nations of the world in the beginning and middle of the present century.

To-day we have fleets engaged in transporting phosphoretic and nitrogeneous materials from continent to continent; the services of the miner and the skill of the chemist are required to supply this food-material to our exhausted fields.

The nitrate mines of Chile, the phosphate beds of South Carolina and Florida, of Belgium and Russia, the mountains of apatite rock of Estremadura and the deposits of the same material in Canada, the potash salts of Germany and Hungary, are drawn into the service of agriculture. One of the most gigantic branches of the chemical industry has been built up in order to balance the debit and credit page of the rational farmer in the records of his culture.

But in seeking for remedies that will preserve the fertility of our fields, it is a remarkable fact that a vast amount of waste material which lies right at our feet, is not given a thought.

It is true that all the more valuable waste materials, such as bones, tankage, cracklings, cottonseed meal, leather, hoofs, horns, etc., have a stable market. But the poorer and much more abundant materials have been, and are now, almost entirely neglected.

We will to-night direct our attention to the question of the possibility of utilizing the garbage of our city, which, at the present writing, is the subject of much discussion.

Until recently the garbage collected in this city has been used mainly as a feeding material for the fattening of pigs in the outskirts. For sanitary reasons, the Board of Health has banished the piggeries outside the limits of the county of Philadelphia. This is very commendable to free the city of a nuisance, which at the best was a very crude method of disposing of the material, and which, by the carelessness of those who make a business of it, certainly created a health-endangering nuisance; but the decision of the Board of Health made the disposal of the material very much more difficult than before.

The city of Philadelphia is divided into five districts for the collection of garbage. During the summer months, from June to September, the accumulation of a single district runs up to 100 tons per day, while in the other months of the year the daily output varies, and in the middle of the winter falls to twenty-five tons per day.

A general average for the whole year is about 250 tons per day for the whole city.

This estimate we can safely use for calculation of returns but not as a basis for the construction of a plant, for which the maximum figures will have to be taken.

For the first district, comprising all that part of the city south from South Street, from river to river, a furnace for the cremation of garbage has been erected, situated on Washington Avenue and Twentieth Street.

Unquestionably cremation is the most complete system for destroying all organic substances, and doubtless to the extreme sanitarian the only method that should be adopted.

But what about the economical results? The daily operation of the furnace requires labor and fuel, the product of a cremator is a small quantity of ashes and worthless at that. Four or five per cent. of ashes is all that remains of the garbage when incinerated.

The American Incinerating Company, with headquarters at Washington Avenue and Twentieth Street, has offered its product to the fertilizer trade. I have here a sample of these ashes which were sent to us. Our analysis yielded us:

Total phosphoric acid = 15·32 per cent. (= 33·88 per cent. phosphate of lime), potash 0·25 per cent., soluble in water.

I was astonished to find so little potash but the intense heat in the furnace has driven off a part of the alkalies as chloride vapors, otherwise the analysis should show at least four times as much.

This ash, even with fifteen per cent. phosphoric acid, has a very low market value because natural phosphates in bags, and ground to the finest powder, can be laid down at our doors at $5 per ton.

The phosphoric acid of such low percentage is valueless for dissolving purposes because it will only yield practically a powder containing five to six per cent. of available phosphoric acid. This low product cannot be used for mixing fertilizers and it cannot be offered to the market when acid rocks containing thirteen to fourteen per cent. of available phosphoric acid are offered as low as $10 to $12 per ton.

The products of the cremating process, therefore, will never become a commercial article. The question then arises, Can the same sanitary requirements be reached in another way? Without doubt they can, and, at the same time, the valuable constituents of the garbage destroyed in the furnace can be saved.

The city garbage, embracing all the refuse from the table and kitchen, changes its qualities considerably with the season. Just now we are in the vegetable period and the results of my experiments represent about the lowest results obtainable.

The experiments I have made are not laboratory experiments, but practical manufacturing experiments, handling at a time from six to twelve tons of material. I have been in the fortunate situation of being able to utilize, at intervals, apparatus designed for other purposes but very well adapted for the purpose of these experiments.

There is no secrecy about the principle of rationally utilizing garbage, and there are no new processes involved for which enormous patent fees will have to be paid.

The process is divided in two main operations:

(1) The separation of the grease by extraction.

(2) The drying of the remainder to form directly a salable product.

The results I have obtained yielded me about seventeen per cent., on an average, of dry product from garbage tankage, a sample of which you have before you. This dry tankage is a very excellent fertilizing material. Its composition is:

	Per Cent.
Moisture,	4·41
Organic matter, (including 4·3 per cent. NH_3)	73·34
Mineral matter,	22·25
	100 00

On a smaller scale than that which could profitably be carried on in Philadelphia, garbage is utilized successfully in this way in several places. I have received from Detroit samples of fertilizer made from garbage with as high as 5·37 per cent. ammonia, 6·08 phosphoric acid; and, at another time, 3·76 per cent. ammonia, 3·36 phosphoric acid.

A specimen from Providence contained 3·55 ammonia, 3·38 phosphoric acid; from other places, 3·86 ammonia, 3·51 phosphoric acid.

A fair average analysis, showing the minimum and maximum of what we may export, is as follows:

	Per Cent.	*Per Cent.*
Ammonia,	3 50	4·50
Phosphoric acid, (corresponding to phosphate of lime, 6·54, 13·28)	3·	6·
Water soluble potash,	0·25	0·50

At the present market price the unit of ammonia is sold at 2·60. This would give, for the low grade, a market value of $9.10 per ton; for the high grade, $11.10 per ton.

It is safe to say that at the present market these products will realize $10 per ton. I leave phosphoric acid and potash out of the calculation to give you the practical valuation.

This material is a most excellent fertilizer, not only chemically but also physically, and its usefulness in the manufacture of fertilizers is without limit.

The amount of garbage tankage produced from a ton of material as gathered up from the houses, placed at the lowest percentage (viz: about fifteen per cent.), amounts to 300 pounds per ton. One hundred tons per day will give 30,000 pounds or fifteen tons daily.

Taking the daily average of one district, we will average seven and one-half tons, or 2,250 tons per year; and for the five districts, 11,250 tons, having a market value of $112,500.

Now, let us see what we restore to the fields in this amount of products.

The ammonia taken at four per cent. in one ton of the tankage contains eighty pounds of this important plant food, and 112,500 tons, or the amount of production from the garbage of this city should be equivalent to a saving of 9,000,000 pounds of ammonia, 9,000,000 pounds of phosphoric acid, and 500,000 pounds of potash.

All of this has been taken from our fields, and, if wasted or destroyed, represents so much loss to the community at large, but if this amount be regained and restored in proper form to the farm and garden it means so much saving. All of this amount must be restored from other sources in some way. If any waste material is worth saving it is surely the garbage of the cities, as I have endeavored to show.

There is another feature connected with this waste, viz: the regaining of the grease contained in garbage.

City garbage, at a low estimate, will yield three per cent. of a black grease, which you see in the samples before you. Even for this black grease, there exists a limited market at low figures for lubricating purposes (for car wheels). This black grease rarely contains much free fatty acid but it is by no means free from it. I have had samples containing over six per cent.

If the regular production should rise to such quantities as the garbage of the whole city will permit of producing, other uses must be found for this product, which, in the crude state has but a limited field of usefulness. There are ways and means known to the chemist, however, to improve this raw product, and the refined material made from it will readily find a market in competition with other greases.

The result of a chemical artifice of this kind, I take pleasure in introducing to your notice in the sample before you. The method employed by me in this work is absolutely practical in respect of quick action, cheapness and positive results.

The grease stock so produced is very oily at 60° F. It yields about seventy to seventy-five per cent. of this very fine oil which will find a ready sale. This oil will prove a puzzle to the best expert in the analysis of oils, for it contains traces of all oils and greases which enter the kitchen. It will challenge the reliability of all the color tests, the iodine numbers, etc., but in spite of its evasion of the methods of a Mailliau and Benedikt, it will find an excellent market.

The refined grease is a very fine soap stock, and a very crude product of a test in that direction I have with me. This soap is made solely from the same grease you have before you.

The rational mode of disposing of the city garbage is as simple as anything can be.

First, to gain all the grease, we must apply practical methods of extraction by known solvents; then, to save the fertilizer materials, we must employ the most rapid and economical methods to expel the eighty per cent. of water contained in the material.

Small amounts are easily handled; the difficulty arises when such enormous quantities stare one in the face. It is not, therefore, so much the chemical processes employed as the proper disposition of the plant, which must be well understood.

The stock delivered at the works must disappear in the process, on its arrival, and must never be permitted to rest for a moment until, after forty-eight hours, it is ready to be filled into bags for shipment in the form you see before you in this sample. It is no more difficult to handle the enormous quantities of garbage than it is to handle the animal refuse of our city.

My experience of many years in handling materials of this kind in enormous quantities, first in Chicago, and since 1877 in this city, as the chemical manager of the largest works of its kind, permits me to speak advisedly on this subject, and I am prepared to stake my reputation as a technical chemist on the assertion that the utilization of our city garbage can be carried on as a financially successful operation for the saving of the valuable materials contained therein. How important the solution of this question is for the city of Philadelphia is well illustrated by the constant discussion of the subject in the daily papers.

Cremation, as I have shown, produces, at considerable expense, a valueless product. The rational chemical process yields, at no more cost, products which make a large figure in the housekeeping of a community.

Should we cast aside the warnings of an economist like Carey? Shall the teachings of Liebig and of all the prominent agricultural chemists of all nations have been in vain? I trust not, and believe not.

In this century of progress, with our knowledge of chemistry, and with the most complete machinery at our disposal, it seems to me like a lapse into barbarism to destroy this most valuable material simply for the purpose of getting rid of it, while at the same time, we are eager to obtain these very same materials for our fields by purchase from other sources.

There is no doubt in my mind that this question of the disposal of our garbage can be solved by careful consideration of all points, by practical business men, to the advantage of the city authorities and the contractors for this work, to the fullest satisfaction of the health authorities, and to the benefit of the farmer.

Capital intelligently invested should be productive, not destructive. Instead of spending thousands of dollars for the erection of crematories to destroy, let us erect sanitary chemical works to preserve, this valuable material. There can be no danger to the public health in the conduct of a rational system for the utilization of garbage. All microbic carriers of contagious sicknesses are destroyed by a temperature of 212° F., and this dry product you have before you is as harmless to the public health as the flour in the barrel.

My desire and expectation to-night, in making this presentation of an important industrial and sanitary problem, is to receive the endorsement of the Section, and later on, that of the Institute, to have you condemn the destruction of these valuable waste products, and approve, as the only right solution of this question, the preservation of these products displayed before you by a rational process of manufacture such as that indicated above.[*]

ARTESIAN WELLS.

BY OSCAR C. S. CARTER.
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[*Read at the stated meeting of the Chemical Section, held March 21, 1893.*]

Within the last few years a great many artesian wells have been drilled in Pennsylvania to obtain pure drinking water for towns, villages and farms, and also for various manufacturing and industrial purposes, such as the manufacture of artificial ice, the brewing of beer and for use in steam and locomotive boilers. The two principal questions to consider in artesian water are the quality and the quantity. First, as regards the quality, there can be no doubt that water which filters through from 200 to 500 feet of rocky strata is free from all deleterious organic matter. Disease germs, which sewage in river water renders so common, are unknown in artesian water unless the well be drilled in a thickly populated district or be improperly cased. Artesian water comes to the surface clear and sparkling and is never muddy from clayey matter or dirt held in suspension. The geological formations of Southeastern Pennsylvania contain prolific water-bearing strata. Wells drilled in the sandstones, clay slates, and shales of the trias, in the mica schists and gneisses of the Philadelphia group, in the Silurian limestone and in the Potsdam sandstone, generally yield an abundance of water; occasionally, a barren locality is met with, but this is rarely the case. It would be impossible to lay down any hard-and-fast rule as to which formation furnishes the most abundant supply of water; an examination of the records of the accompanying wells will give some idea. The new red sandstone shales and slates and the mica schists of the Philadelphia group yield an abundant supply of water. The Silurian limestone in this vicinity often dips steeply, but gives a good supply. Thus far, wells drilled in the Potsdam sandstone have not yielded as much water as the above formations, although a good supply is obtained. It may be stated as a rule that those stratified rocks which are highly jointed, fissured and porous, furnish many easy channels for the passage of rain-water to strata situated at great depths, and that beds of clay, clay slates, fine-grained sandstones, quartzites and compact mica schists make very good confining beds. The quantity of water furnished by deep wells near Philadelphia is enormous. The well at Lansdale, Montgomery County, can yield 288,000 gallons per day; the two wells at Jenkintown, 216,000 gallons each per day; the well of the Oriental Bath Company, 1104 Walnut Street, 144,000 gallons per day. One popular error seems to have gained a foothold, that a well is of little interest unless it be a deep one, and that the deepest ones furnish the most water. Many lose sight of the fact that the object of drilling a well is to obtain water, and when an abundant supply is reached at a moderate depth it is a useless expense to drill deeper. Shallow wells often yield enormous quantities of water. A drilled water well only 35 feet deep and 6 inches in diameter, at Washington Square gives over 1,500 gallons per hour and does not lower no matter how much is pumped. (See *Proc. Amer. Philos. Soc.*, May 1, 1891.)

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[*] The very able report on the above paper, which appeared in the *Public Ledger*, seems to have given to some persons interested in this question, the wrong impression, that it was presented in the interest of the company with which I am connected. Such is not the case.

This question, like any other question of interest to the company, has been fairly examined into by its chemical manager, but the company, for business reasons, would not undertake the utilization of garbage.

The chemical manager, therefore, was at liberty to make use of the results of his experiments for the benefit of the public at large, and did so after consultation with the president of the company and with his approbation.

B. T.

What kind of Rocks yield Hard Water and what kind Soft?—Whether a water be hard or soft depends mainly upon the composition of the soil and rocks through which it filters. Water that passes through calcareous or magnesium rocks of great thickness will probably be hard, while water that passes through rocks composed of silica, alumina, iron, potash or soda will probably be soft. The great deposits of limestone, marble, gypsum and other calcareous rocks, as well as the magnesian rocks, such as dolomite, chlorite and talcose schists would then yield hard water. The granites, gneisses and many sandstones and slates would furnish soft water. This, in the main, is true, although there are some exceptions which local conditions modify. Some sandstones will yield soft water, while other sandstones furnish hard water; it depends mainly upon the cement which binds the grains together; if the cementing material be carbonate of lime or sulphate of lime the water will probably be hard, especially if the well be of great depth and the water be long in contact with the rocks. If, on the other hand, the cementing material be feldspar, such as orthoclase or albite (not labradorite), or even gelatinous silica, the water will probably be soft.

In England, many determinations of the hardness of spring and artesian water from different geological formations have been made; so that it can be safely predicted what kind of water an artesian well will yield when it is drilled in the Devonian, in the Silurian limestone, in the new red sandstone, or in the chalk.

DEEP ARTESIAN WELL WATER (*England*).

	Hardness.	
Water from Devonian sandstone,	17°	Hard waters.
Water from magnesian limestone,	43°	
Water from new red sandstone,	17°	
Water from chalk,	27°	

Water from granite and gneiss, soft.
Water from Silurian sandstones, slate and shales, soft.
Water from millstone grit, soft.

Water which flows through calcareous channels is hard, while that which flows through silicious rocks is soft.

The same facts are noticed in the artesian wells of Pennsylvania. Artesian water from the new red sandstone is generally hard, though not so hard as the English new red water. An analysis of a new red water from a well 102 feet deep, at Norristown, gave me 11°·8 of hardness; the hardness was mostly due to carbonate of lime, although some sulphate was present. The magnesian limestones of Pennsylvania furnish hard water; this is noticeable at Reading, Pa., where a limestone stream empties into the Schuylkill and neutralizes the water from the coal mines, which is charged with sulphate of iron and a little sulphuric acid. When the streams meet, sulphate of lime is precipitated, and also carbonate of iron, which decomposes to ferric hydrate, and can be seen as a brown stain on the dam near the city.

Many of our deep marble and limestone quarries of Montgomery County, Hitner's, Henderson's, Graver's, Rambo's and others, are always partially filled with water; this is not rain-water because at Graver's quarry the rotary force pumps were running eight months of the year night and day, with an eight-inch and four-inch discharge pipe and the quarry was not nearly pumped dry. This water filters through the limestone and is not always hard because at Rambo's quarry the water was used in the boilers and the engineer reported no scale or precipitate present. Deep artesian water from clay slates and shales of the trias is often a little hard. (See analysis of boiler scale from Lansdale artesian well water.) Deep artesian wells in the mica schist and gneiss of Philadelphia and vicinity furnish water of slight hardness; this hardness disappears when the well has been in use for several months and is not sufficient to interfere with its use for industrial purposes. The purest and clearest water in this vicinity would be obtained by drilling in the syenite and granitic rocks. The water that issues from the granitic rocks and hills above Lafayette Station is of exceptional purity and is free from organic matter.

Rate of Drilling different Rocks.—The rate of drilling through the various rocks, such as granite, syenite, mica schist, hornblende schist, sandstone, limestone, clay slates and shales, is a very important and interesting feature as a saving of time and expense depends on it. There are several factors that enter in the problem of rapid rock drilling, the most important perhaps are the hardness and compactness of the rock, and the weight, temper and drop of the drill. The most difficult rocks to drill through are trap, quartzite, compact fine-grained sandstones, certain clay slates, granites, syenites and compact hornblende schist, obsidian, etc.

The softer rocks, such as talcose and chlorite schists, serpentine and other magnesian rocks, limestone, dolomite, hydro mica schists and many coarse-grained sandstones are readily drilled through. The following table will show the thickness of rock pierced by a chisel drill 20 feet long $5\frac{5}{8}$ inches in diameter, weighing 700 pounds, guided so as to make a round hole:

Locality.	*Rock.*	*Rate.*
Duffield's farm, on Stony Creek, near Belfry, . . .	Clay Slate (Trias),	4½ feet drilled in 10 hours.
Ice Company's well, Norristown, ...	Sandstone (Trias),	5 " "
Kunkle's farm, Valley Green Road, near Flourtown,	Limestone (Silurian),	5½ " "
Wheadley's farm, Chester County, ...	Hydro Mica Schist,	7 " "
Wm. Janeas farm, near William Station, ...	Sandstone (Potsdam),	10 " "
Roberts well, Spring Mill, ...	Sandstone (Potsdam),	18½ " 7 hours.

The Potsdam sandstone at the above localities is not like the hard edge hill rock and conglomerate, but on the contrary is soft and micaceous, which accounts for the rapid progress. When the Schuylkill Valley Railroad was built the Pennsylvania engineers found the hardest rock they had to drill along the Schuylkill was the trap rock at Conshohocken; the next hardest was the syenite, below Spring Mill. One contractor forfeited his contract on that account; next came the mica schist, then the sandstone, and last the limestone. The minerals which compose a rock may be very hard, and yet the cementing material may hold the grains so loosely that the drill will make rapid progress through the rock. Sandstone, when composed entirely of silica, or when the cementing material is gelatinous, silica as in quartzite, is extremely hard to drill, but when the cement which binds the grains is feldspar, which decomposes readily, then the grains are loosely held, and the rock is readily drilled. The hardness of a steel drill is over 7, while the hardness of the minerals which go to make up the great mass of rocks is under 7. Feldspar, 6; hornblende, 5 to 6; augite, 5 to 6; mica, 3; limestone, 3; dolomite, 3½; talc, 1; quartz, which has a hardness of 7, is the most abundant mineral, and rapidly wears and destroys the temper of a drill. Coarse-grained rocks are more readily drilled than fine-grained. Steeply-dipping strata are more difficult to drill on account of the trouble in keeping the drill vertical. Sayer's well, at Fox Chase, was drilled in the mica schist. There was one vein of rock in this well, probably quartz, only seven inches in thickness, that took eighteen hours to drill, and required twelve sharp drills in that time.

Cryolite in a Philadelphia Artesian Well.—Wm. W. Matos, a student of the Central High School, presented me with two specimens of minerals, which he said came from an artesian well; on examination, they proved to be cryolite. One specimen contained several rhombohedra of siderite, which frequently accompanies Greenland cryolite. The other specimen contained, besides cryolite, some siderite, galenite, quartz, and a little copper pyrites, all of which are found in the cryolite of Ivigtuk, Greenland. The specimens were about the size of common marbles. On telling him that it was unusual to find cryolite except in Greenland and a few other localities, and that there must be some error he volunteered to see the driller again and question him closely. The specimens are without doubt cryolite. The exact locality of the well is about Fiftieth Street and Columbia Avenue, on land belonging to Pennsylvania Railroad. The well was drilled by Brush & Co., a New York firm. On asking why the specimens were not ground to powder by the drill, he said that when drilling at a depth of 280 feet they struck a water crevice, and the drill fell a short distance and broke off some fragments of the surrounding rock, these were drawn up by the sand pump, and the specimens of cryolite were among them. The driller says the cryolite was broken into several small pieces, and estimates the depth at which it was broken off to be about 280 feet. He thinks the vein is only a few inches in thickness. The well was drilled to obtain water for the locomotive engines of Pennsylvania Railroad Company. The rock passed through was mica schist and gneiss, and at and around 280 feet the driller pronounced the rock very hard. The diameter of the well is six inches, and they quit drilling at a depth of 350 feet. The water rises in the wall to within twenty-five feet of the surface of the ground, and on pumping without a force pump, and using only a small engine pump, the well yields 2,400 to 3,000 gallons per hour; it would give much more with an improved pump. No specimens were found below 280 feet. The finder was Mr. Richard Wickward.

Cost of Artesian Wells.—The price of drilling is about $2 per foot in Montgomery County for wells 6 inches in diameter and from 100 to 200 feet deep: this is independent of the character and hardness of the rock. A hard clay slate requires twice as long a time to drill as a loose mica schist or a decomposed sandstone, and yet it would be a difficult matter to regulate the price according to the hardness of the rock and the difficulty of drilling, because in many wells alternate beds of sandstone, red shale and sometimes clay are met with. An examination of the table on the rate of drilling will show that the rate with which different rocks are drilled varies greatly yet the same rate per foot is charged for granites, syenites, mica schists, sandstones and limestones. I have known the drillers to make the unusually slow progress of six inches in ten hours when a very hard quartzite was being drilled. Sometimes they are delayed more than a month over the usual time required to drill a well, by some unusual obstruction, such as a hard, steeply-dipping stratum, when it is almost impossible to keep the drill vertical and the well straight; occasionally, the tools become loosened and drop down the well, and a week or more is wasted in grappling for them. The six-inch iron pipe (internal diameter five and five-eighths inches), which is used to line the well, varies in price from forty to fifty-five cents per foot. Most of the wells in Montgomery County, which will be referred to later, and whose depth varies from 50 to 200 feet, were drilled at the rate of about $2 per foot. The driller of these wells guarantees water, and promises to finish the well and test it or no pay. If the water should be chalybeate or colored, which is rarely the case, he agrees to pump it until it becomes clear.

In Philadelphia, the charges vary and contracts differ in terms. Some drillers contract, for a certain specified sum, to drill a well that will furnish a certain amount of good water per minute, generally fifty or seventy-five gallons. The contract price includes everything, casing, coal and testing.

Many of the Philadelphia wells are double-cased; the first pipe put down is an eight-inch pipe; then a six-inch pipe is put down inside of this, and the space between the two is filled with hydraulic cement.

Some contracts have been made at the rate of $4 per foot, this includes the drilling, casing, testing and everything connected with the well.

Other contracts have been made at the rate of $2.75 per foot for drilling down to 500 feet and $3 per foot for drilling below a depth of 500 feet; this does not include the iron pipe for casing, but only the drilling.

Deep Artesian Wells in the Red Shales and Clay Slates of the Triassic.—At Lansdale, Montgomery County, Pa., on the line of the North Penn Railroad, three artesian wells were drilled for Effrig & Son, pork packers.

The first well is 159 feet deep, the second one 376 feet, and the third and latest one is 611 feet deep. These wells are within fifty feet of one another. The last well has 259 feet of iron pipe as casing, and, on pumping with a small pump, gives seventy gallons per minute; with a larger and improved pump, it will give 200 gallons per minute, or 288,000 gallons per day: the supply seems to be practically inexhaustible. The water rises to within 140 feet of the top of the well.

No systematic record of the borings was kept. Rock was first struck at a depth of twelve feet.

The drill passed through alternate layers of red shale, red sandstone, blue clay slates, and black carbonaceous slates. A small bed of carbonaceous slate, six or eight inches thick, was struck, and also a bed of the same character, twenty feet thick. This last bed was found at a depth of forty feet from the surface. Under this bed of black clay slate was a deposit of what they supposed to be cannel coal, but it was evidently a shale or slate, very rich in carbon.

The water from these wells when used in boilers deposits a scale, which I analyzed and found to consist of $CaCO_3$, $MgCO_3$, $CaSO_4$, $MgSO_4$, NaCl, and a trace of iron, sufficient to color slightly the scale. The water is not very hard, the hardness being mainly due to $CaCO_3$, which makes up the bulk of the scale. This hardness of the water is only temporary and will disappear when the well has been in use for several months and continually pumped, as fresh water takes the place of that which has long been in contact with rocks and which has dissolved out the salts of lime and magnesia. This I have noticed to be the case in several wells; when the well is first drilled, the water is hard enough to require a small amount of soda in the boiler as an anti-incrustator. It acts by precipitating the lime and softening the water. After the well has been pumped for several months the hardness disappears and the anti-incrustator is dispensed with.

The 611-foot well was six months in drilling. The drillers complained that the clay slate was very hard and contained much quartz, which kept them drilling much longer than usual.

The above facts correspond well with those obtained from another well drilled a few miles from Lansdale on, the Duffield farm, between Custer and Belfry, on the Stony Creek Railroad. (See *Proc. Amer. Philos. Soc.*,vol. xxix, May 25, 1891.) In this last well, the bed of very black rock, supposed to be coal, was found at a depth of about forty feet from the surface; this is the same depth as the Lansdale bed. I understand the same bed of coaly rock was found when Mr. Rozenzi drilled the very deep well in Bucks County for gas. Another firm drilled the Duffield well, and they made the same complaint about the hardness of the rock. One bed in particular, that was supposed to be quartzite, was so hard that only six inches of it could be drilled in ten hours. The Duffield well is only sixty-five feet deep and yields but sixty gallons per hour, while the Lansdale well yields 200 gallons per minute. In these tightly-packed clay slates an abundance of water is found only at great depths.

Deep Artesian Well in the Mica Schist of Philadelphia.—This well was drilled at the Gladstone Hotel, Eleventh and Pine Streets, to obtain water for drinking and household purposes. This well, at the time of writing, December, 1892, is not finished. The present depth of the well is 576 feet; the first forty-four feet passed through was clay and gravel, then the usual mica schist rock was struck. No drillings were preserved, but two specimens of rock broken off by the drill were kept, one at a depth of ninety feet, the other at a depth of 240 feet. The first specimen proved to be hornblende crystallized; the second specimen was mica schist, composed of biotite mica, feldspar and large grains of transparent quartz. I am doubtful about the depth of the first specimen, and think it must have come from a much greater depth than ninety feet, assigned by the driller because no hornblende was seen in any of the pumpings of the well drilled by the Oriental Bath Company, of 1104 Walnut Street. This well was 265 feet in depth, and the drillings were carefully preserved for about every ten feet. The second specimen corresponds with the rock found at nearly the same depth at the Walnut Street well. The first specimen was a mass of a pure hornblende, and may be regarded as an accessory mineral of the mica schist rock, and not as hornblende schist. The well yields 5,100 gallons per hour, and with an improved pump will give over 6,000 gallons per hour. The water rises to within thirty-one feet of the surface, which corresponds closely with the Green Street and Walnut Street wells. On pumping forty-eight hours, or 244,800 gallons, the water falls from the height of thirty-one to fifty-one feet, or a drop of twenty feet in forty-eight hours, It remains at fifty-one feet from the surface no matter how long it is pumped.

Deep Artesian Wells in the Mica Schist at Jenkintown.—The two wells at Jenkintown were drilled for the purpose of supplying drinking water to the town, and also the surrounding country for a distance of three miles; in this they were eminently successful.

The present depth of the first well is 324 feet; of the second well, 349 feet. They are only eight feet apart. They are both cased for a distance of forty-five feet with iron pipe. The two wells at present are connected. The second well was at first only 270 feet deep, but was afterwards drilled to a depth of 349 feet. On deepening this well they struck at 310 feet a fissure or crevice, which connects the two wells. Before the wells were connected, the water rose to within thirty-eight feet of the surface in the first well, and within sixty feet of the surface in the second. At present they both stand at the same level. The wells yield 9,000 gallons each per hour, and by constant pumping for fifteen hours the fall is 150 feet.

Artesian Well in the Mica Schist of Philadelphia.—This well was drilled at the northwest corner of Twenty-fourth and Green Streets, to obtain water for the manufacture of artificial ice. The well is eight inches in diameter and was drilled to a depth of 300 feet. The well was cased with iron pipe to a depth of thirty feet and afterwards to sixty feet, but it is the intention of the company to case it to a depth of 120 feet.

The water rises to within twenty-six feet of the surface. At the well drilled by the Oriental Bath Company, of 1104 Walnut Street, the water rises to within twenty-eight feet of the surface. The Green Street well yields about 5,160 gallons per hour, while the Walnut Street well yields 6,000 gallons per hour.

The drillings of the Green Street well were not preserved.

The Montgomery County wells are nearly all six inches in diameter and when lined with iron pipe they are five and five-eighths inches in diameter.

The motive-power is a twelve horse-power engine. The beam is fifteen feet in length, the drill bar three inches in diameter. The drill has a drop of eighteen inches.

Artesian Well in the Trias at Norristown, Pa.—This well was drilled on the top of Sandy Hill, a very high hill which overlooks Norristown and the Schuylkill Valley. The drilling was commenced in the bottom of an old dry well, fifty feet in depth, on the property of John T. Dyer.

56—Sandstone,	to 56
6—Dark red shale,	" 62
6—Red shale micaceous,	68
2—Sandstone, light colored transparent quartz, abundance of silvery muscovite,	70
5—Red shale,	75
5—White sandstone muscovite, quartz and pink orthoclase,	80
2—Same,	82
2—Pink sandstone, more pink orthoclase,	84
2—White sandstone, finer grained,	86
5—White sandstone orthoclase, quartz, very little mica,	91
4—Red shale, no mica,	95
5—Red shale, slightly micaceous,	100
2—Red sandstone, fine grained,	102
2—Gray sandstone, little mica,	104
8—Light red sandstone, orthoclase, quartz and muscovite,	112
2—White sandstone, feldspathic,	114
2—Red shale,	116
9—Red sandstone, feldspathic,	125
5—White sandstone, very fine grained, little mica, feldspar missing,	130
5—Dark red sandstone, micaceous,	135
5—Dark red sandstone, slightly micaceous,	140
5—White sandstone like 130, resembles sea sand,	145
5—White sandstone, very fine grained, only little feldspar,	150
10—Pink and white sandstone, orthoclase and muscovite,	160
9—Pink and white sandstone, muscovite and more orthoclase,	169

Very few water crevices were met with, the first crevice was at a depth of seventy-four feet, no water was struck again until a depth of 167 feet was reached. The well was tested when a depth of 121 feet was reached, and was pumped dry in seven minutes, this water mostly came from the first crevice at seventy-four feet. When the depth of 169 feet was reached the well was again tested and yielded 900 gallons per hour, after four hours' steady pumping the water did not lower.

The water rises in the well to within seventy-four feet of the surface. This is rather remarkable when we consider that the hill is a steep one and the well is within a short distance of the slope; many predicted that little water would be found on such a high hill.

Artesian Well in the Silurian Limestone near Lancasterville, Montgomery County, Pa.—This well was drilled on the property of H. F. Hallman. The drilling was commenced in an old well, which was already sixty-four feet in depth.

64 feet	to	64
11—Limestone,	"	75
4—Blue limestone,		79
6—Gray limestone,		85
9—White limestone,		94
2—White limestone, slightly micaceous,		96
2—Gray limestone, slightly micaceous and silicious,		98

Crevices were met with at seventy-nine feet, and four or five between eighty-five and ninety-four feet. The rock was very loose, and the water rises to within sixty-four feet of the surface. The well yields 600 gallons per hour, after five hours' continuous pumping the level does not lower any.

Artesian Well in the Trias Red Shale, Jeffersonville, Montgomery County, Pa.—This well was drilled on the property of of F. A. Poth, and passed through a bed of red shale, forty-six feet in thickness.

10—Clay,	to	10
5—Sandstone,		15
15—Gray sandstone, feldspathic,		30
10—Same,		40
5—Red shale, micaceous,		45
5—Red shale, coarser, more mica,		50
5—Red shale, lighter color, little mica,		55
14—Red shale, very dark in color, much red hematite,		69
6—Red shale, softer micaceous,		75
11—Red shale, dark red, fine grained, micaceous,		86
6½—Sandstone, gray feldspathic, micaceous,		92½

This well was not tested by the drillers, but Mr. Poth put down a deep well steam pump with a capacity of thirty gallons per minute. It is the opinion of the driller that the well yields twenty gallons per minute. Water was first struck between thirty-five and forty feet, and small crevices were met with below this.

Artesian Well in Trias between Norristown and Jeffersonville.—Well drilled on the property of the West End Land Company, about two miles from the Trenton limestone, which outcrops at Mogee's Station, along the Schuylkill.

10—	Yellow sandstone, crumbling,	to 10
10—	Same,	20
10—	Red shale, micaceous,	30
7—	Red sandstone, micaceous,	37
11—	Brown sandstone, micaceous,	48
3—	Gray sandstone, much gray feldspar, some mica,	51
2—	Gray sandstone, fine grained, micaceous and feldspathic,	53
22—	Red sandstone, micaceous and feldspathic,	75

The well yields 1,500 gallons per hour, and does not lower after four hours' pumping.

This well was about two weeks in drilling.

Artesian Well in the Trias Hickorytown, Montgomery County:

5—	Clay,	to 5
5—	Decomposed sandstone,	10
30—	Light yellow sandstone,	40
30—	Yellow sandstone feldspathic (orthoclase),	70

Below seventy feet is a bed of white sandstone, containing muscovite and orthoclase. Water was first struck at fifty-six feet. The well yields 600 gallons per hour and the water rises to within forty-five feet of the surface.

Artesian Well in the Lowest Trias at Bridgeport, Montgomery County.—This well was drilled in the sandstone not far from the Silurian limestone of the Chester Valley, on the property of Chas. Meyers.

4—	Clay,	to 4
21—	Sandstone (decomposed),	25
6—	Sandstone, coarse grained, light color, trace of mica,	31
9—	Red shale, rich in Fe_2O_3,	40
12—	Sandstone, light color, transparent quartz, slightly micaceous,	52
13—	Sandstone, fine grained, micaceous,	65

The well yields 600 gallons per hour, and after pumping five hours does not lower any.

Artesian Well in the Potsdam Sandstone near Fort Washington.—This well was drilled on the property of J. Conrad, on the Bethlehem Pike, one-half mile from Fort Washington, near the site of Washington's old fort. The rock dipped steeply and it was difficult to keep the well straight.

1½—	Soil,	to 1½
13½—	Potsdam sandstone, coarse grained, fawn colored,	" 15

15—Potsdam sandstone, fine grained, fawn colored,	to 30
22—Potsdam sandstone, fine, slightly micaceous, darker colored,	" 52
4—Potsdam sandstone, fine, slightly micaceous, fawn colored,	" 56
8—Potsdam sandstone, fine grained, slate colored,	" 64

Water was first struck at depth of fifty-two feet and rose ten feet in the well. The well yields 600 gallons per hour, and on pumping five hours does not lower any.

Artesian Well in the Trias, Sandy Hill School House, Whitpain Township.—

6½—Sand,	to 6½
6½—Sandstone,	13
7—White sandstone, decomposed orthoclase,	20
13—Same, no mica,	33
2—Same,	35
5—Gray sandstone, some clay,	40
10—Red shale,	50
4—White sandstone, highly feldspathic,	54
4—Sandstone and clay, lead colored, micaceous,	58
2—Decomposed shale (clayey),	60

Water first struck at forty feet. The rock changes without any crevices until between fifty-four and sixty feet, when a little more water enters the well. The water rises to within twenty-eight feet of the surface. The well can be pumped dry in thirty minutes on pumping five gallons per minute. It will only yield two gallons per minute without lowering, according to the driller.

Artesian Well at Shady Grove School House, near Skippack Pike, and Morris Road, in the Trias.—

1½—Soil,	to 1½
3½—Decomposed sandstone,	" 5
5—Sandstone, coarse grained, light color (conglomerate),	10
8—Sandstone, finer grained, feldspathic, slightly micaceous,	18
6—Sandstone, coarse, highly feldspathic, much decomposed,	24
6—Same,	30
5—Red clay, derived from feldspar,	35
5—Red shale, slightly micaceous,	40
5—Red clay,	45

This well was about four days in drilling. The rock was very open from fifteen to twenty feet and it was difficult to keep any water in the well and there were small crevices in almost every change of rock, but they did not yield water. Water was first struck at twenty-four feet and rose to within nineteen feet of the surface. The well yields 900 gallons per hour and on pumping three hours and twenty minutes does not lower any.

Artesian Well in the Silurian Limestone, near Williams Station, Plymouth Railroad.—This well was drilled on the property of Thomas Phipps.

11—Soil and clay,	to	1
2—Limestone,		13
7—Limestone, coarse, yellow,		20
10—Same,		30
13—Same,		43

Struck water at sixteen feet. The rock was very loose and kept dropping in the well until harder rock was reached at twenty feet. It was necessary to case with iron pipe to twenty-three. Three crevices were met with from twenty feet to forty-three feet. The water stands at sixteen feet from the surface. The well yields 900 gallons per hour and does not lower on pumping four hours. This limestone is highly magnesian, and on analysis I find it contains a little strontium.

Water Well drilled in the Trias, at Washington Square School House, Montgomery County.—

3—Soil,	to	3
4—Sandstone,	"	7
7—Fine grained, red shale, micaceous,	"	14
5—Coarse red shale, micaceous,		19
9—Sandstone, very coarse, mica and feldspar,		28
10½—Red clay,		38½

Below thirty-eight and one-half is a bed of red shale. First crevice was met at a depth of twenty-five feet and the water rose to within fourteen feet of the surface. The well yields 600 gallons per hour and on pumping four hours the water does not lower any. The red clay probably holds the water.

Water Well Drilled in the Trias, at Belfry, Stony Creek Railroad.—This well was drilled at St. John's Lutheran Church.

10—Red shale,	to	10
10—Red shale, deep color, little mica, much Fe_2O_3,	"	20
5—Red shale, lighter color, finer grained, less micaceous,		25
5—Brown shale, hard, fine scales of mica in abundance,		30
2—Sandstone, brownish, gray, micaceous,		32
5—Sandstone, brown,		37

This shallow well yields only thirty gallons per hour; 100 gallons per hour would pump it dry. The water rises to within fifteen feet of the surface. Only one small water crevice was struck and that was at twenty feet. The drillers abandoned this well; the reason it was not finished was because it was impossible to keep the well straight. It started to go crooked at twenty-two feet and continued so all the way down. Every method known to the drillers was tried, but it was impossible to keep it straight. The water was a little hard. No charge was made for drilling.

[*Proceedings of the stated meeting, held Tuesday, September 19, 1893.*]

HALL OF THE FRANKLIN INSTITUTE,
PHILADELPHIA, September 19, 1893.

DR. WM. H. GREENE, President, in the chair.

Mr. J. Benjamin Glavin, 1312 Passyunk Avenue, proposed for membership by Dr. Wahl at the June meeting, was duly elected.

Dr. Wahl also proposed the name of Mr. C. E. Martin, chemist to the house of James Martin & Co., 125 Chestnut Street. At the close of the meeting Mr. Martin was duly elected to membership.

Bills amounting to $93.20, covering items of subscriptions to journals and expenses of addressing and mailing section notices, were approved by vote and ordered to be paid.

The report of the committee appointed to prepare a memorial of the late Conrad J. Semper, was read, accepted and ordered to be spread upon the minutes. (The memorial is printed as an appendix to these minutes.)

Mr. Pemberton read an interesting and carefully prepared paper on "The Determination of Phosphoric Acid by the Titration of the Yellow Precipitate with Standard Alkali." The paper was very favorably commented upon by Dr. Terne and briefly discussed by him and the author.

Professor Smith followed with a paper on "The Atomic Weight of Molybdenum," prepared jointly by himself and Mr. Philip Maas. It was discussed by Mr. R. A. Fisher, the President, and the author. Both papers were referred for publication in the *Journal.*

The meeting then adjourned. WM. C. DAY, *Secretary.*

CONRAD J. SEMPER.

In the death of Conrad J. Semper, which occurred on June 12, 1893, the Chemical Section has suffered the loss of one of its estimable members, who, though his name does not appear as a contributor to the published volumes of its proceedings, was nevertheless a frequent attendant of its meetings and always exhibited a lively interest in its welfare.

Mr. Semper was a son of Gottfried Semper, a distinguished architect, and received his early education at the Polytechnic School at Zürich, completing his studies in chemistry in Berlin, Freiberg, Tübingen and Heidelberg.

In the year 1865, Harrison Brothers & Co., of Philadelphia, being in need of the services of a chemist conversant with a certain branch of manufacture in which they were interested, requested their agents in Germany to aid them in securing a competent person. Through these gentlemen the request was conveyed to Dr. Zürich, who was then Director of the Laboratory of the Prussian Government, and who suggested his assistant, Mr. Semper, for the position. This suggestion resulted in Semper's engagement by the firm.

This engagement proved to be a permanent one, and was fulfilled with such mutual satisfaction that Semper, in due course, became the chemical manager of the house, which post he continued to occupy until his death.

His professional work was naturally confined to the development and improvement of methods and processes connected with the business of manufacturing chemicals and colors, in which the house of Harrison Brothers & Co. occupy the first rank among American manufacturers, and to this congenial work he directed all his energies, and, though no serious contributions to professional literature appear to have come from his pen, the records of the Patent Office bear testimony to his activity and originality in his chosen sphere of work.

His most important technical work appears to have been in connection with the study of the treatment of beauxite for the commercial production of alumina salts especially in the development of the reactions of metallic dioxides (such as those of lead and manganese) upon ferruginous solutions of alumina, for the removal of iron. In this work he was associated with Dr. Constantine Fahlberg, well-known as the discoverer of saccharin.

The house, in whose service his life was spent, bears the following warm testimony to his professional skill: "The late Mr. Semper was without doubt a very able chemist, and, when occasion required, showed great genius. His attention was given generally to our various manufactures, and we regarded him at all times as the fountain source of our chemical knowledge." To this we may add the cordial testimony of his business and professional friends, that his excellent judgment in the planning and erection of buildings and apparatus, and his great experience and eminently practical turn of mind, made him a sound adviser and capable director, whose place it will be difficult to fill.

Personally, Mr. Semper was most amiable in disposition and endeared himself to a wide circle of friends. A widow and three sons survive him.

[SIGNED]
DR. BRUNO TERNE,
WM. H. WAHL,
H. PEMBERTON, JR.

[*Proceedings of the stated meeting held Tuesday, October 17, 1893.*]

HALL OF THE FRANKLIN INSTITUTE,
PHILADELPHIA, October 17, 1893.

DR. D. K. TUTTLE, Vice-President, in the chair.

Dr. Wahl proposed the name of Mr. L. F. Kebler, chemist to Smith, Kline & French Company, manufacturing chemists, 305 Cherry Street, Philadelphia. The name was referred to the Committee on Admissions and Mr. Kebler was duly elected.

A letter from Miss Lizette A. Fisher to Dr. Wahl, announced the death of our fellow-member, Mr. R. A. Fisher, on October 6th. Dr. Tuttle appointed Mr. H. Pemberton, Jr., to prepare a suitable minute of the sad event.

Mr. Boyer suggested that such lectures of the Institute's general course, as were of special interest to chemists be made a part of the proceedings of the Section. Dr. Wahl stated that such a plan would be highly desirable, but its execution would be attended with serious expense to the Section, such expense being incidental to publication.

Dr. Wahl remarked, further on, the desirability of making the selection of lecturers on chemical topics, a duty of the Section. The president and others concurred in the views expressed by Dr. Wahl.

Dr. Hooker then read a paper "On the Azines of the Lapachol Group," and followed it with another on "The Change from Ortho- to Para- and from Para- to Ortho-Quinones." The papers were listened to with much interest, and were afterwards informally discussed by the author and Dr. Hall, Prof. Smith and Dr. Keiser. Beautifully crystallized specimens of the substances treated of were submitted for inspection.

A paper entitled "Experiments on Slag Cements," by Mr. R. W. Mahon was, in the absence of the author, read by title and referred for publication.

Adjourned. WM. C. DAY, *Secretary*.

THE DETERMINATION OF PHOSPHORIC ACID BY THE TITRATION OF THE YELLOW PRECIPITATE WITH STANDARD ALKALI.

BY HENRY PEMBERTON, JR.

[*Read at the stated meeting of the Chemical Section, held Sept. 19, 1893.*]

In the year 1882, I described a process for determining phosphoric acid, volumetrically, by ammonium molybdate, on the principle of Wildenstein's sulphuric acid determination, or of Gay Lussac's silver method. An *aqueous* solution of ammonium molybdate is run into the solution of the phosphate until no further precipitate is formed.

But it is not of this process that I now have to speak. It is referred to here, in order to draw attention to the concluding paragraph of the paper, as follows:

"I have obtained very sharp and accurate results by determining the amount of yellow precipitate (formed as above, after thorough washing), by means of a standard solution of caustic alkali, using litmus as an indicator; a description of which I hope to present in a future paper. I mention it here simply to place the fact on record." (*Journ. Frank. Inst.*, **113**, 193; *Chem. News*, **46**, 7.)

At that time I did a considerable amount of work upon the last-mentioned process, with very satisfactory results. A study was made of the conditions most favorable to obtaining a phospho-molybdate precipitate of constant composition, using solutions of di-sodic hydric phosphate of known strength, and also a solution of apatite, the determinations being checked by standard methods.

Before the process was in shape for publication, however, my attention was called to work of an entirely different nature, and no description of the method was published other than that embodied in the above-quoted paragraph.

Since that time several chemists have described processes based upon the same principle.

E. Thilo, in the analysis of Thomas slag (*Chem. Ztg.*, **11,** 193), dissolves the yellow precipitate in standard ammonia, and titrates back with acid, using litmus as an indicator.

Franz Hundeshagen (*Zeit. Anal. Chem.*, **28,** 171) uses standard sodium hydrate in excess, and titrates back with nitric acid, using phenolphthalein as an indicator.

C. E. Manby (*Jour. Anal. and Appd. Chem.*, **6,** 82) determines the phosphorus in steel, iron and iron ones, by dissolving the yellow precipitate in ammonia, acidifying with nitric acid, evaporating to dryness, and heating gently to expel nitric acid and ammonium nitrate. He then titrates, using the same solution and indicator as Hundeshagen employs.

James O. Handy (*Jour. Anal. and Appd. Chem.*, **6,** 204) avoids the evaporation and heating and titrates directly as Thilo and Hundeshagen do, using standard soda and phenolphthalein. M. Rothberg and W. A. Auchinvole (*Jour. Anal. and Appd. Chem.*, **6,** 243) also describe the same process.

Although it is now eleven years since I drew attention to this process, its advantages are so great that any information touching it, in addition to that furnished by the foregoing chemists, may be of interest. It far surpasses in quickness the process described by me (on the Gay Lussac or Wildenstein principle) and at the same time lacks nothing in accuracy. In most of the papers of the above-mentioned chemists, the process is applied to the determination of phosphorus in small quantities, as it occurs, for instance, in iron, steel or ores. During the past year, I have had occasion to apply it to the examination of a number of phosphate rocks, as well as of strong solutions of phosphoric acid, containing over fifty per cent. P_2O_5 and the method has been used continuously during that time. I am indebted to Mr. Edwin Harris, who had charge of most of the laboratory work of the factory, for many of the figures given below. It was seldom that two tests of the same material differed more than 0·1 per cent. in P_2O_5 even when the total P_2O_5 present amounted to as much as forty per cent. to fifty per cent. of the substance analyzed.

The following solutions are used:

Ammonium Molybdate.—Ninety grams of the crystals are dissolved (in a large beaker) in somewhat less than one litre of water. This is allowed to settle, overnight, and the clear liquor decanted into a litre flask. The small quantity of insoluble molybdic acid, always present, is dissolved in a little ammonia and added to the main solution. Should the molybdate be found to contain traces of P_2O_5, a few decigrams of magnesium sulphate are added, ammonia being added to faint alkalinity. The whole is then made up to one litre. It is this *aqueous* solution that is used, *no nitric acid whatever being employed.* Each cubic centimetre precipitates three milligrams of P_2O_5.

The *ammonium nitrate* solution is simply a saturated aqueous solution of the salt. Distilled water is poured into the bottle of crystals in quantity *in*sufficient to dissolve them all. Even in cold weather, ten cubic centimetres of this solution is amply sufficient for each test.

The *nitric acid*, used for acidifying the solution of the phosphate, has a specific gravity of 1·4, or thereabouts.

The *standard potassium hydrate* solution is of such strength that 1 cc. = 1 mgr. P_2O_5. One hundred cubic centimetres of it will neutralize 32·65 cubic centimetres of normal acid. It can be made from normal potassium hydrate (that has been freed from all carbonate, by barium hydrate), by diluting 326·5 cubic centimetres to one litre. But its strength is best determined empirically by a direct test upon a phosphate solution of known strength, precipitating with ammonic molybdate and making the analysis as described below, all carbonate of potassium having first been removed by barium hydrate.

The standard acid has the same strength, volume for volume, as the potassium hydrate, and can be made by diluting 326·5 cubic centimetres of normal acid to one litre. In testing it against the alkali, phenolphthalein (and not methyl orange) should be used.

The indicator can be either litmus, rosolic acid, or phenolphthalein. I have used the latter almost exclusively, as it has been shown, by J. H. Long (*Am. Chem. Jour.*, **11**, 84), that titrations with this indicator in the presence of ammonium salts are perfectly reliable if the amount of the ammonium salt present is not excessive, if the solution is cold, and if the phenolphthalein is used in sufficient quantity. One gram of the phenolphthalein is, accordingly, dissolved in 100 cubic centimetres of sixty per cent. alcohol, and at least 0·5 cubic centimetres of this solution is used for each titration. The washing of the ammonium phospho-molybdate is done by water. (Isbert and Stutzer, *Zeit. Anal. Chem.*, **26**, 584.) It may be of interest to quote from their results, since it is by some chemists thought necessary to wash with a neutral or acid solution of an ammonium salt. In all tests, as made by them, twenty-five cubic centimetres of the sodium phosphate solution were precipitated by ammonium molybdate and the phosphoric acid determined therefrom, as magnesium pyrophosphate in the usual manner.

When the yellow precipitate was washed with ammonium nitrate solution, there was obtained:

(1) 0·1943 gram P_2O_5 in 50 cc.
(2) 0·1948 gram P_2O_5 in 50 cc.

When washed with *water*, there was found:

(3) 0·1947 gram P_2O_5 in 50 cc.
(4) 0·1942 gram P_2O_5 in 50 cc.

In order to establish the fact more certainly, the precipitate was washed with unusually large quantities of water:

	cc. of water used in washing.	*P_2O_5 found.*
(5)	300	0·1947 in 50 cc.
(6)	400	0·1944 in 50 cc.
(7)	500	0·1948 in 50 cc.
(8)	1,000	0·1940 in 50 cc.

There is, accordingly, no danger of loss in washing the yellow precipitate with water.

The following is the method of performing the analysis:

One gram of the phosphate is dissolved in nitric acid, an excess of which can be used with impunity, and the solution filtered into a 250 cubic centimetre flask and made up to the mark. The solution can even be poured into the flask without filtering, since the presence of a little insoluble matter does not interfere in the least with the titration. Moreover, since most phosphate rocks seldom contain over ten per cent. of insoluble matter, and as this has the specific gravity of at least 2, it occupies a volume of about 0·05 cubic centimetre, an amount so small that it may be neglected. (For instance, even in the case of a phosphate rock containing forty per cent. P_2O_5, the error is only 0·008 per cent. P_2O_5.)

After the clear solution has been poured off, it is well to treat the sand, etc., at the bottom of the beaker, with a cubic centimetre or so of hydrochloric acid, in the warmth, to insure complete solution.

It is not necessary to evaporate to dryness. Isbert and Stutzer have shown, in their paper, that when the yellow precipitate is washed with *water*, the soluble silica is removed, and that evaporation (to render the silica insoluble) is superfluous. Their results are corroborated by the test analysis that will be given below. In the event of its being desirable to remove silica by evaporation, for any purpose, the evaporation should be performed over a water-bath, or, if on an iron plate, with great care, since, otherwise, meta- or pyro-, phosphates are formed with results that are correspondingly low.

Twenty-five cubic centimetres of the solution (equal to 0·1 gram) are now taken for analysis. It may be thought, by some, that an analysis made upon so small a quantity of material as one decigram, and with a standard solution representing only one milligram per cubic centimetre, may be liable to errors that would not exist, when using larger quantities or stronger solutions. But it should be borne in mind that the accuracy of measurement with a twenty-five-cubic-centimetre pipette, is precisely the same, whether ten grams of the original substance are taken or only one gram. Any error in measuring with a pipette is, of course, entirely independent of the quantity in solution. In regard to the amount of material to be manipulated (filtered, washed, etc.) it will be remembered that the weight of the yellow precipitate is over twenty-eight times the weight of the P_2O_5 contained in it. Every milligram of

P_2O_5 is accordingly represented by more than twenty-eight milligrams of precipitate. The standard alkali, although representing only 0·001 gram per cubic centimetre is, in reality more than three times as strong as the decinormal solution generally employed. Of course, in the case of materials containing only ten to fifteen per cent. P_2O_5, as in fertilizers, two or three grams can be taken for analysis, if desired, instead of one gram.

Returning, therefore, to the method of the analysis, twenty-five cubic centimetres of the solution are measured out and delivered into a beaker holding not more than 100 to 125 cubic centimetres. A larger beaker requires unnecessary washing to remove the free acid in washing the yellow precipitate. The solution is neutralized with ammonia—until a precipitate just begins to form—and five cubic centimetres of nitric acid of specific gravity 1·4 added. Ten cubic centimetres of the ammonium nitrate solution are added, and the entire bulk of the solution made up to fifty to seventy-five cubic centimetres by adding water.

Heat is now applied and the solution brought to a full boil. It is then removed from the lamp, no more heat being applied and treated *at once*, with five cubic centimetres of the aqueous solution of ammonium molybdate, which is run into it from a five-cubic-centimetre volume pipette, the solution being stirred as the precipitate is added. The beaker is now allowed to rest quietly for about one minute, during which time the precipitate settles almost completely. The five-cubic-centimetre pipette is filled with the molybdate solution, and a part of its contents allowed to drop in, holding the beaker up to the light. If a formation of a yellow cloud takes place, it is at once perceptible, in which case the remainder of the pipettefull is run in, the solution stirred and allowed to settle. A third pipettefull is now added as before. Should it cause no further cloud, only about one-half of its contents is added, the remainder being run into the beaker into which the filtrate and washings from the yellow precipitate are to go. In the test analyses given below, it will be shown that even when *fifteen cubic centimetres in excess*, of the molybdate, were purposely used, over and above the calculated amount, the results were accurate – no molybdic acid coming down with the yellow precipitate.

It is seldom that more than fifteen cubic centimetres in all (three five-cubic-centimetre pipettefulls) of the molybdate have to be added. Since each cubic centimetre precipitates three milligrams P_2O_5, fifteen cubic centimetres will precipitate forty-five milligrams P_2O_5. This is equivalent to forty-five per cent. on the 0·1 gram taken for analysis, and it is not often that any material to be examined contains over this percentage. In the analysis of materials rich in phosphoric acid, it is one of the embarrassing features of the usual process, in which the *nitric acid solution* of the molybdate is used, that, in the first place, large quantities of the precipitant have to be used (frequently several hundred cubic centimetres), and, in the second place, that the analyst is never certain that enough has been added to throw down all of the phosphoric acid. This necessitates frequent testings of small portions of the phosphate solution, or of the filtrate. There is another difficulty peculiar to the process as usually carried out, in all methods in which the determination is made directly upon the phospho-molybdate itself, in that much care must be observed to keep the solution at a certain temperature, since otherwise molybdic acid contaminates the precipitate and the analysis is rendered worthless. In the process herein described, using an *aqueous* solution of the molybdate, the point at which sufficient of the precipitant has been added is easily seen. No molybdic acid separates, because, in the first place, no great excess of molybdate is added; and because, in the second place, the solution is filtered immediately, or as soon as it has settled, which requires only a minute or two. The time required from the first addition of the molybdate to the beginning of the filtration is never over ten minutes, and is generally less. The filtrate and washings from the precipitate when treated with additional molybdate solution, give, on standing on a hot plate for an hour or so, a snow-white precipitate of molybdic acid, showing that all of the phosphoric acid has been precipitated. I have observed this hundreds of times.

A slight correction should be made to the statement made above in regard to fifteen cubic centimetres of the molybdate precipitating forty-five milligrams of P_2O_5. This is not strictly true, for the reason that a small quantity (something over one cubic centimetre) of the molybdate is required to neutralize the solvent action of the nitric acid. Therefore, in *very* high grade phosphates a fourth five cubic centimetre pipette full may be required.

The yellow precipitate is now filtered through a filter seven centimetres in diameter, decanting the clear solution only. This is repeated three or four times, washing down the sides of the beaker, stirring up the precipitate, and washing the filter and sides of the funnel above the filter each time. The precipitate is then transferred to the filter and washed there. When the precipitate is large it cannot be churned up by the wash water and cannot be washed down to the apex of the filter. This is generally the case when there is over ten or fifteen per cent. phosphoric acid present in the substance analyzed. In such an event, I am accustomed to wash the precipitate back into the beaker, and to fill the funnel with water above the level of the filter, doing this two or three times, then washing the precipitate back into the filter. It is not necessary to transfer to the filter the precipitate adhering to the sides of the beaker.

It goes without saying that during the washing no ammonia must be present in the atmosphere of the laboratory. Inasmuch as the beaker, funnel, filter and precipitate are small, the washing does not take long to perform. It requires, in fact, from ten to fifteen minutes, even when large precipitates (= thirty to forty per cent. P_2O_5) are handled. The precipitate and filter are now transferred together to the beaker. By pressure with the tip of the finger, upon the double fold of the filter, it is easily given a sideways motion and lifted out of the funnel without any danger of breakage, the precipitate being still within it. The alkali solution is run in until the precipitate has dissolved, at least twelve drops of the phenolphthalein (1 : 100) are then added, and the acid run in without delay until the pearly color disappears and the solution is colorless. The presence of the filter paper does not interfere in the least. The reaction of the indicator is not so sharp as when only acid and alkali are used, but it is easy to tell with certainty the difference caused by one drop of either acid or alkali. After deducting the volume of acid used from that of the alkali, the remainder gives the percentage of P_2O_5 directly, each cubic centimetre being equal to one per cent. P_2O_5. Thus, if there are 28·3 cubic centimetres of alkali consumed, the material contains 28·3 per cent. P_2O_5 when one decigram is taken for analysis. From the time the twenty-five cubic centimetres are measured out until the result is obtained, from thirty to forty minutes are required.

I have applied this process to determinations of phosphoric acid in phosphates and fertilizers, and have had no experience in determining phosphorus in iron, steel, or iron ores. I am inclined to believe that in the presence of such large quantities of iron salts when using the *aqueous* solution of the molybdate it may be necessary to guard against contamination of the yellow precipitate by ferric hydrate, perhaps by using larger quantities of nitric acid than five cubic centimetres, and perhaps by washing the precipitate at first, with dilute nitric acid. It may also be the case that the yellow precipitate will form more slowly.

The following analytical experiments were made in order to test the process.

Several phosphate of soda solutions were used at first, the strength of which was only approximately known, as the aim was to see how closely two readings would agree; equal quantities of the phosphate being taken for each pair of tests.

A.

	cc.
(1) KHO with rosolic acid,	15·0
(2) KHO with rosolic acid,	15·15

B.

	cc.
(1) KHO rosolic acid,	30·5
(2) KHO rosolic acid,	30·5
(3) KHO phenolphthalein,	30·7

All titrations, after this, were made with phenolphthalein.

C.

	cc.
(1) KHO,	31·7
(2) KHO,	31·8

A KHO solution was now made of such strength that 1 cc. = 1 mgr. P_2O_5.

D.

	mgr.
(1) P_2O_5,	50·35
(2) P_2O_5,	50·55
(3) P_2O_5,	50·40

E.

	mgr.
(1) P_2O_5,	51·6
(2) P_2O_5,	51·55

F.

	mgr.
(1) P_2O_5,	51·05
(2) P_2O_5,	50·95

D, E and F were solutions used in standardizing.

Two different samples of Florida phosphate rock were examined.

I.

	Per Cent.
(1) P_2O_5,	= 29·68
(2) P_2O_5,	= 29·84

II.

(1) P_2O_5,	= 31·28
(2) P_2O_5,	= 31·34

The following were solutions of phosphoric acid:

I.

	Per Cent.
(1) P_2O_5,	= 46·78
(2) P_2O_5,	= 46·69

II.

(1) P_2O_5,	= 44·41
(2) P_2O_5,	= 44·63

III.

(1) P_2O_5,	= 48·95
(2) P_2O_5,	= 48·80

The effect of *an excess* of ammonium molybdate was tried. The soluble part of an acid phosphate was made up to a definite volume and fifty cubic centimetres taken for analysis. It was found to contain 8·28 per cent. P_2O_5. The test was repeated, using fifteen cubic centimetres of the molybdate more than was used in the first trial. Result = 8·36 per cent. P_2O_5 equal to a difference of 0·08 per cent.

The following tests show that it is not necessary to remove silicic acid, by evaporating to dryness before precipitating with the ammonic molybdate.

A sample of Florida phosphate rock contained:

	Per Cent.
(1) P_2O_5 silica removed,	31·21
(2) P_2O_5 silica not removed,	31·21

Another sample of the same rock was also tried:

Silica removed :	*Per Cent.*
(1) P_2O_5,	= 30·5
(2) P_2O_5,	= 30·7
Average P_2O_5,	= 30·6

Silica not removed :	*Per Cent.*
(1) P_2O_5,	30·6
(2) P_2O_5,	30·7
Average P_2O_5,	30·65

When silica is not removed the filtrate from the yellow precipitate has a yellow tinge.

The relation between the P_2O_5 in the precipitate and the potassium hydrate was established by determining the strength of a solution of disodic hydric phosphate by precipitation as the ammonium-magnesium salt, and also by testing it by this titration process. The phosphate of soda solution was *weighed* (not measured), and the magnesia precipitate, after filtering, was dissolved and reprecipitated with ammonia. (Gooch, *Am. Chem. Jour.*, **1**, 405.) The results are given in Table I, the last column giving the amounts of P_2O_5 obtained on a basis of ten grams of the solution:

TABLE I.

	Weight of Na_2HPO_4 Solution. Grams.	*Weight of $Mg_2P_2O_7$ Obtained. Grams.*	*Equal to P_2O_5. Grams.*	*Grams P_2O_5 in 10 Grams of Solution.*
I,	75·824	1·2471	0·7956	0·10494
II,	101·167	1·6637	1·0614	0·10492
III,	101·622	1·6733	1·0676	0·10505
Average,				0·10497

Therefore, ten grams of the solution contain 0·10497 gram P_2O_5.

Weighed portions of the same solution were now precipitated with molybdate and the precipitate titrated with alkali. The results are given in Table II, the last column of which gives the number of cubic centimetres of alkali equivalent to ten grams of the solution. The indicator was phenolphthalein:

TABLE II.

	Weight of $Na_2H.PO_4$ Solution. Grams.	*Number of cc. of KHO Sol. Required.*	*= Number of cc. KHO Sol. Required for 10 Grams Solution.*
I,	7·4975	79·05	= 105·4
II,	7·8255	82·40	= 105·3
Average,			= 105·35

It follows, therefore, that 105·35 cubic centimetres alkali = 0·10497 gram P_2O_5, therefore,

(1) 100 cubic centimetres alkali = 99·64 milligrams P_2O_5.

The HCl solution was now titrated against the alkali, using phenolphthalein as the indicator. 99·00 cubic centimetres alkali were found to equal 99·05 cubic centimetres acid.

The HCl was then standardized against pure sodium carbonate.

(With methyl orange, cold:)

(*a*) 1·1291 grams Na_2CO_3 = 65·45 cubic centimetres HCl

(With phenolphthalein, boiling:)

(*b*) 1·1934 grams Na_2CO_3 = 69·2 cubic centimetres HCl

Therefore, 100 cubic centimetres =

(*a*) 1725· milligrams Na_2CO_3
(*b*) 1725· milligrams Na_2CO_3

Since 99·00 alkali = 99·05 acid, it follows that:

(2) 100 cubic centimetres alkali = 1726 milligrams Na_2CO_3

It has already been shown by (1) that 100 cubic centimetres alkali = 99·64 milligrams P_2O_5. Therefore, combining (1) and (2) we obtain 99·64 milligrams P_2O_5 = 1726· milligrams Na_2CO_3.

Dividing each by its molecular weight, we have:

for P_2O_5, ... $\frac{99\cdot64}{142\cdot06} = \cdot7014$

for Na_2CO_3, ... $\frac{1726}{106\cdot1} = 16\cdot27$

Therefore $P_2O_5 : Na_2CO_3 = 0\cdot7014 : 16\cdot27 = 1 : 23\cdot2$.

In other words, 23·2 molecules of Na_2CO_3 are required to neutralize the yellow precipitate containing one molecule P_2O_5.

The above figures are based upon the following atomic weights:

Mg, ... = 24·3
O, ... = 16
P, ... = 31·03
Na, ... = 23·05
C, ... = 12

$$Mg_2 P_2O_7 = 63\cdot80 \text{ per cent. } P_2O_5.$$

There is some uncertainty as to the correct atomic weight of magnesium. If Mg = 24 (instead of 24·3 as taken above) with $Mg_2P_2O_7$ = 63·98 per cent. P_2O_5 the ratio of Na_2CO_3 to P_2O_5 = 23·1 to 1 (instead of 23·2 to 1). It is difficult to obtain *absolutely* pure Na_2CO_3; any impurity in it will make the ratio of Na_2CO_3 to P_2O_5 too high.

Practically, therefore, twenty-three molecules of Na_2CO_3 are required for one molecule P_2O_5. This agrees with Hundeshagen's results.

I have never seen any explanation as to why twenty-three molecules of alkali are required to neutralize one molecule of the ammonium-phospho-molybdate. A discussion of the subject, therefore, may be of interest. Hundeshagen has shown (*loc. cit.*) that (neglecting any water of crystallization) the yellow precipitate, after thorough washing with water, has the following composition:

$$\begin{array}{r} PO_4 \\ 12\ MoO_3 \\ 3\ NH_4 \end{array}$$

Or, doubling the formula, for the sake of clearness:

$$\begin{array}{c} P_2O_8 \\ 24\ MoO_3 \\ 6\ NH_4 \end{array}$$

R. T. Thomson has shown in his researches on indicators (*Chem. News*, **47**, 127) that of the three hydrogen atoms in H_3PO_4 two must be saturated with alkali before the reaction with phenolphthalein will be neutral. The next drop of alkali after this causing the red color to appear. Writing the formula differently, $H_6P_2O_8$ must become $R_4H_2P_2O_8$ (R being the radical NH_4, or any alkali metal). Therefore, when the yellow precipitate is broken up by alkali, only four of the six molecules of NH_4 are required to form (with the P_2O_5 of the precipitate) a phosphate of ammonium that is neutral to the indicator. The remaining two molecules of NH_4 unite with one molecule of MoO_3, yielding also a salt that is of neutral reaction. This leaves twenty-three molecules of MoO_3, representing the "net available acidity" (if I may use the expression) of the ammonium-phosphomolybdate. These twenty-three molecules of MoO_3, of course require twenty-three molecules of Na_2CO_3 (or its equivalent of KHO) to form Na_2MoO_4. Q. E. D. The following is the formula representing the reaction ·

$$\begin{array}{c} 6NH_4.\ P_2O_8.\ 24MoO_3 + \\ 23Na_2CO_3, + H2O, = (NH_4)_4.\ H_2P_2O_8 + \\ (NH_4)_2MoO_4 + 23Na_2MoO_4 + 23CO_2 \end{array}$$

It may be well to give a short *résumé* of this method. One gram of phosphate rock, or two or three grams of fertilizer are dissolved in nitric acid, and without evaporating to dryness diluted to 250 cubic centimetres. The solution need not be filtered. Twenty-five cubic centimetres of the solution are delivered into a four-ounce beaker and neutralized with ammonia—until a precipitate just begins to form—and then treated with five cubic centimetres of HNO_3 of 1·4 specific gravity. Ten cubic centimetres of a saturated solution of ammonium nitrate are added and the solution diluted to a volume of fifty to seventy-five cubic centimetres.

It is then brought to a full boil, removed from the lamp and five cubic centimetres of the *aqueous* solution of ammonium molybdate added. This is followed by a second and a third five cubic centimetres, if necessary, the precipitate allowed to settle, and filtered at once through a seven centimetre diameter filter. It is washed *thoroughly* with water by decantation and on the filter. The filter and precipitate are transferred bodily to the beaker. Standard alkali is then run in and at least 0·5 cubic centimetre of phenolphthalein (one per cent. solution) added, and then standard acid, until the color vanishes. Each cubic centimetre of alkali equals one milligram of phosphorus pentoxide.

THE METHODS OF TESTING FATS AND OILS.

BY DR. ERNEST MAILLIAU.
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[*Read at a special meeting, held June 8, 1893.*]

Dr. WM. H. GREENE, President, in the chair.

Dr. MAILLIAU spoke as follows:

GENTLEMEN:

The French Government and the Regency of Tunis have taken the opportunity of the great American World's Fair to bestow upon us the honor to communicate to you by conference and by practical experiments the analytical methods which we use in France to recognize the purity of the fatty bodies. I hope that you will give us your kind indulgence and facilitate our modest efforts with the good-will which you have already shown to all our fellow-countrymen who have come to you with the disinterested object of strengthening the scientific bonds which unite the two republics.

If the French and Tunisan Governments have chosen me for their representative, it is only because I direct the ministerial laboratory of technical tests founded for the purpose of studying all the products of the colonies and Mediterranean district, and especially oils and fatty matters as well as the different products which are connected with them, and that I have acquired some knowledge of the subject by long practice and continual investigations.

This is the only laboratory of its kind, and has been placed at Marseilles, the great seaport of France and port of entry for colonial products.

The difficulties of chemical analyses of fatty matters are greatly increased, not only by the slight differences which characterize the various glycerides, but also by the numerous cases of isomerism, and the phenomena of oxidation and fermentation which modify their molecular structures, by the resins and the essential oils which they contain, and also by the foreign matters which injuriously affect them, and the composition of which varies infinitely according to the nature of the soil from which the plant draws nourishment, by the method of extraction, age, and a thousand other causes needless to mention.

Since the methods of communication have been facilitated, and exchanges have become more numerous, the different markets of the world have been flooded with fatty matters presenting different characters though of the same nature as those to which industry and commerce have been accustomed.

We have been led to seek methods of analysis for oils not by their impurities, which vary according to their origin, but by the examination of their principal constituents which remain practically the same for the same species.

For example, it is now well known, and we state with pleasure, since we have made the first of these observations, that the olive oil of Tunis, Morocco and other provinces often present the character of adulterated oils if analyzed without proper precautions, or by old processes.

Accordingly, the greater number of governments and large companies have been obliged to modify their specifications to control the purchases necessitated by their wants by methods better adapted to the needs of commerce and the progress of science. Accordingly, before trying the action of chemical reagents upon this product so extremely variable and alterable, it is indispensable for obtaining precise results to submit the material to a purification preceded and followed by a number of filtrations. By thus removing the impurities which when present alter the results, we bring back the fatty bodies of the same species to a type which is always practically the same. To reach this end we work sometimes by washing with hot distilled water, sometimes with strong or dilute alcohol, sometimes we refine the fatty matter by the use of caustic soda lye (containing ten per cent. sodium hydrate), employed in the proportion of ten per cent. of the fat. The emulsion is poured upon a saturated solution of sodium chlorid and by the action of gentle heat, the different parts separate and the clear oil holding in suspension insoluble particles of soap rises quickly to the surface.

It is well to note that fatty matter, even when neutral, as has been demonstrated. dissolves notable quantities of alcohol, which must be eliminated, if this method of washing has been employed. The process of the operation cannot be fixed definitely; it varies according to the nature of the impurities and the object of the research.

It is certain, for example, in determining the amount of volatile acids we must be content with the simple filtration, and that when examining the oils of the cruciferæ we must not use caustic soda which changes organic sulphur to a soluble sodium sulfid. Having finished the preliminary operations, we may, according to circumstances, operate directly on the neutral fat or the fatty acids prepared from it.

The fatty acids collected in the nascent state (that is to say, when they rise to the surface in a pasty mass) have much stronger chemical affinities than when melted and de-hydrated. This difference is particularly remarkable in the examination of cotton-seed and sesame oils, the black and red colorations obtained very clearly with a mixture of five per cent. upon the nascent fatty acids are not visible with the same fatty acids when melted.

The purification skilfully made does not destroy the chemical characters of the oil, as is easy to verify, by treating comparatively the same oil containing five per cent. of the fatty matter, the presence of which we wish to demonstrate. The reactions of the added material are in general intensified by these different treatments.

By working upon the fatty acids of the neutral oils, I have been able to demonstrate the purity of certain fatty matters which appeared adulterated and in which the presence of cotton-seed and sesame oils were indicated by the old methods which I have been able to revise.

(*Circulaire du Ministre de la Marine Française*, en date du 26 Juillet, 1892. *Rapport du Résident-général de Tunisie*, en date du 9 Mai, 1892. *Circulaires des Ministres du Commerce et de l'Agriculture*, etc.)

I well know that in practice these preliminary operations may appear very tedious, but I do not advise their use except in cases where adulterations have been indicated by the usual methods, and it is desired to make the proof positive.

Besides, I cannot understand why a chemist has always been expected in the analysis of such delicate materials as fats, to discover an infallible reagent, a single drop of which will immediately turn olive oil green, peanut black, sesame red, etc., so that any inexperienced person could discover adulteration and bring the perpetrator to justice. This requirement, of the most difficult part of verification, is absolutely incomprehensible and is only to be excused by the ignorance of those who ask it.

We will now proceed to the study of each oil in particular. We will pass rapidly over those which possess only a secondary interest, so as to lay greater stress upon those which are the object of a great number of sophistications, as for example, olive oil. But in the first place we will indicate rapidly the general processes, physical and chemical, which are used for the identification of the various fats.

GENERAL METHODS.

(1) *Specific Gravity.*—Specific gravity is taken with accuracy by the Mohr balance, which is too well known to need description. It must be borne in mind that the specific gravity of the same fat varies greatly with individual sam-

ples, and this physical character is not sufficient to allow us to decide on purity or adulteration.

(2) *Action of Nitrous Fumes.*—We owe to a Marseilles gentleman, M. Poutet, the first serious proposition for recognizing certain adulterations of olive oil. It was designed especially to discover the presence of poppy-seed oil, with which at that time, olive oil was very frequently adulterated, and for which the process gave good results.

It is based upon the transformation of the olein to its isomeric modification elaidin, by the action of nitrous fumes. It has been modified by other chemists, Messrs. Boudet, Faure and Cailletet. The process of Mr. Cailletet was most sure and simple, and we use it in the following manner:

We take a tube 10 cubic centimeters long, $2\frac{5}{10}$ cubic centimetres wide, in which are twenty cubic centimeters of the fat to be analyzed. Six drops of pure sulfuric acid at 66° B. are added, the tube shaken one minute and then nine drops of nitric acid C. P. 40° B. are added, after which the tube is again shaken and then plunged in boiling water, where it is left exactly five minutes, after which it is cooled in a water-bath at 8° to 10° C., whence it is taken at the end of two hours, and the condition of the mass observed. It is well to note the different colorations obtained. First, after the addition of the sulfuric acid; second, after the addition of nitric acid; third, after the removal from the water-bath, and fourth after chilling.

(3) *Sulfuric Saponification.*—M. Maumené proposed to observe the rise of temperature produced by rapidly mixing sulfuric acid with oil. The manner of applying the process in our laboratory is as follows: fifty grams of the fat for analysis are weighed into a conical glass of 100 cubic centimeters capacity. The temperature is noted and ten cubic centimeters sulfuric acid, 66° B. at the same temperature as the oil, is added. The two liquids are stirred together for one minute. An accurate thermometer is then immersed in the upper portion of the mass, stirred slowly, and the maximum temperature noted. The initial temperature must be at least 20° C. In order to obtain exact results

it is well to make several determintions and take their mean, when the variation does not exceed 2° C.

To obtain the relative sulfuric saponification, we note the rise of temperature obtained with fifty grams of distilled water at the same temperature as the oil and ten cubic centimetres of the same sulfuric acid. The number of degrees obtained by the oil is multiplied by 100 and the product divided by the number of degrees obtained with water. This process has the advantage of giving results nearly constant with acids of somewhat different strength. I have tried the application of the sulfuric saponification with semi-solid vegetable oils, by working at 2° or 3° above their melting points, and the results have been very satisfactory, especially for palm-nut oil and cocoanut oil, because the differences between them and the fluid oils often amount to 45° or more, as, for example, between palm-nut oil and sesame oil.

(4) *Iodin Number.*—In the fatty bodies there are members of unsaturated series, as, for example, oleic acid, which can absorb into its molecule as many atoms of the halogens as there are lacking atoms of hydrogen for complete saturation. The iodin number of olive oil varies between 80 and 84, that of peanut oil is 97, while that of cotton-seed oil is 108. These differences then allow, within certain limits, the determination of the purity of the various fats. We apply the Hübl method as follows:

Solutions required :

Alcoholic solution of iodin, ...	50 grams.
Solution of hyposulfite of sodium, ...	24·8 grams per litre.
Solution of mercuric chlorid, ...	60 grams per litre.
Solution of potassium iodid, ...	100 grams per litre.

Five grams of fatty acid are weighed out, diluted to 100 cubic centimeters with alcohol ninety-two per cent.; ten cubic centimeters of the solution are taken and to it added twenty centimeters of the iodin solution and fifteen to twenty cubic centimeters of the solution of mercuric chlorid. The flask is closed and allowed to stand three hours. Twenty cubic centimeters of the potassium iodid solution are added and the excess of iodin titrated. When the brown coloration begins to disappear a few drops of starch solution are added and then hyposulfite until color disappears.

We will pass in silence the other indices, such as that of acetyl, which is of use only to discover castor oil.

(5) *Freezing Point.*—The freezing point is easy to determine by means of a thermometer and a freezing mixture.

(6) *Melting Points of Fatty Acids.*—The dry and melted fatty acids are sucked into a capillary tube. After solidification the tube is placed beside the bulb of a sensitive thermometer and immersed in a beaker of water, the temperature of which is raised very slowly.

The reading of the thermometer is taken the instant the body passes from the solid to the liquid state.

(7) *Solidification Point of Fatty Acids* (*Titer.*)—The dried and melted fatty acids are placed in a tube 15 centimeters long and 2 centimeters in diameter, which is suspended in a wide-mouthed bottle with a perforated stopper. A thermometer graduated to tenths is inserted so that the bulb reaches the centre of the material. At the moment solidification commences a circular movement is given to the thermometer, stirring the whole mass; the thermometer is then left at rest and carefully watched till the mercury ceases to rise, the reading then taken gives the point of solidification, or titer, conventionally adopted.

(8) *Saturation.*—We operate on five grams of the melted and dried fatty acid with a solution of normal caustic soda. The number of cubic centimeters absorbed give the saturation number.

(9) *Solubility in Absolute Alcohol.*—We determine this in the following manner: the fat is neutralized by agitating in a closed separating funnel for thirty minutes with twice its weight ninety-five per cent. alcohol. After settling it is drawn off and the alcohol held in solution driven off at low temperature, after which it is agitated at 15° C., or at a few degrees above the melting point; or if solid at 15°, with twice its weight of absolute alcohol. A known quantity of this alcohol is evaporated, the residue weighed, and the quantity of oil dissolved by 1,000 grams of alcohol is calculated.

FLUID VEGETABLE OILS.

Olive Oil.—Olive oil, like other vegetable oils, is a mixture of neutral glycerids, olein, stearin, palmitin, etc., and a variable quantity of free fatty acids. It is the edible oil *par excellence*, and the south of France owes a portion of its prosperity to the cultivation of the olive tree. This culture is to-day almost precarious in certain countries, though the consumption continually increases and olive oil always enjoys the just title of uncontested superiority. We can only attribute these remarkable results to the adulterations made for the purpose of selling under the name of olive oil, seed oils, or adulterated olive oils. We would be easily freed from these adulterations if chemists had at their disposition absolutely sure means to recognize them. Unfortunately the similarity of composition and reaction of the various vegetable oils render the demonstration of their presence extremely difficult. In face of the prejudice caused by adulteration, the greatest efforts have been made to solve the problem, and although the results have not been sterile they have not yet reached a satisfactory solution. It is necessary to say that if certain adulterators succeed in selling seed oils disguised as olive, they reverse the problem for the chemist by making him seek olive oil in seed oil. I may remark that the fraud is not always so great, very often the proportion of seed oil is not higher than ten per cent. Consequently, for our methods of analysis to be considered absolutely good, they must give results without recourse to comparisons which are satisfactory to show five per cent. in a mixture. Under these conditions we will be certain to discover adulteration when made in the proportion of ten per cent.

Let us rapidly review the general processes for the recognition of arachide, sesame, cotton-seed and poppy oils in olive oil; and we must acknowledge that none of them demonstrate less than ten per cent.

Specific Gravity.—The specific gravity of olive oil varies from ·915 to ·918; we have ·917 to ·918 for undecorticated peanut; ·921 for decorticated peanut; ·923 for sesame; ·921 to ·924 for cotton-seed oil; ·924 for poppy oil. These variations of density in the olive oil do not allow us to recognize a mixture with any degree of certainty.

Action of Nitrous Fumes.—When taken from the water-bath, if the oil contains a fairly large proportion of peanut oil, it will appear wine-red. Pure olive oil is, on the contrary, lemon-yellow. When taken from the cold bath a complete solidification is observed with pure olive oil, which has the appearance of very light fresh butter; with a mixture of fifteen per cent. of all other oils there is no solidification. This method gives good means of detecting peanut and poppy oils in edible oils, but is of less use when applied to oils used for industrial purposes, which may not solidify, though pure.

Sulfuric Saponification.—The rise of temperature of olive oil is 35°; the relative, 94°. A rise of temperature above 35° usually indicates adulteration, equal or lower results do not absolutely indicate purity, because certain pure olive oils give only 31°, 32° and 33°, and, in consequence, after the addition of seed oil, show only 34° to 35°.

Indices.—The iodin number varies from 80 to 85, and in a certain measure helps us to discover seed oils. It likewise offers us a quantitative method with a mixture of known oils. The variations in composition of the same oil vitiate its sensitiveness for determining mixtures from five to ten per cent.

We will not mention the other general processes, but will dwell particularly on the special reactions which characterize the presence of three oils most frequently used to adulterate olive oil, to-wit: peanut, sesame and cottonseed.

These processes have a much greater analytical value than the general ones, for if in the course of analysis we find unsatisfactory results with the latter, we can detect adulterations with certainty by the former.

Examination for Peanut Oil.—The density is almost the same. The sulfuric saponification, and above all, the Cailletet process gives us good results, but only the presence of arachidic acid $C_{22}H_{44}O_3$ (melting point, 75°) allows the sure recognition of the presence of peanut oil.

We have adopted, with slight modifications, the method of Renard. Twenty grams of the oil are saponified by twenty cubic centimeters of a caustic soda solution of 36° B., diluted in 100 cubic centimeters, alcohol ninety per cent. The soap formed is precipitated by a fifty per cent. solution, in alcohol, of lead acetate which must be neutral. After complete precipitation, decant while warm, and wash the residue with alcohol, which after being ground in a mortar is agitated with 200 cubic centimeters of ether. This operation is repeated three times to remove the last traces of lead oleate soluble in ether. The residue is then put in a porcelain dish containing two or three liters of distilled water and fifty cubic centimeters hydrochloric acid. When decomposition is complete the solution is decanted and the fatty acids washed with distilled water, after which they are dried in an oven to remove the last traces of water, when they are dissolved in forty cubic centimeters of ninety per cent. alcohol. A drop of hydrochloric acid is added and the mixture chilled to 15°. Peanut oil gives a generous deposition of arachidic acid crystals. These are washed twice, using twenty cubic centimeters each time, of ninety per cent. alcohol, then three times with twenty cubic centimeters each time of seventy per cent. alcohol, in which arachidic acid is completely insoluble. The washing is complete when a few drops gives no residue on evaporation. The acids are warmed slightly and treated with boiling absolute alcohol. After filtration the alcohol is evaporated in the oven at 100°, till the weight of the residue remains constant. If the melting point of the residue is between 73° and 75° we can affirm the presence of peanut oil. We must be sure of the freedom of the fatty acids from all traces of oleic acid, which prevents their crystallization. This elaborate but truly scientific process must be carried out only by skilled hands.

Examination for Sesame Oil.—To recognize sesame oil in olive oil we can use the specific gravity, the sulfuric saponification and Cailletet process, but especially the method which we use in our laboratory, and which consists of the reaction of hydrochloric acid and sugar upon the fat.

We do not operate on the glycerid, but on the derived fatty acids. If the oil is operated on directly, we can obtain a red or pink coloration with a perfectly pure olive oil. I have frequently observed this coloration in my laboratory with olive oils from Tunis, Algiers, Molfetta, Bitonto (Italy), and more rarely with those from Provence. This coloration comes from the coloring matter dissolved in the juice which flows out along with the oil from the presses. This can be shown by treating the separated juice with hydrochloric acid and sugar, with which it gives a coloration exactly resembling that given by sesame oil. It is therefore of the highest importance to work with pure fatty acids, according to the process I am about to describe, and which has been called the Milliau process.

Method of Operating.—We saponify fifteen cubic centimeters of the fat under examination with ten cubic centimeters of the solution of caustic soda, 36° B., with the addition of ten cubic centimeters ninety-two per cent. alcohol. When the boiling mixture becomes clear we add 200 cubic centimeters hot distilled water and boil to expel the alcohol; then decompose with ten per cent. sulfuric acid. The fatty acids are removed from the surface in the pasty state and washed by shaking in a test tube with cold distilled water, after which they are heated in an oven to 105°. When the greater part of the water is eliminated and they commence to melt, we pour them on half their volume of pure hydrochloric acid, which has been saturated in the cold with finely pulverized sugar. The mixture is shaken violently in the test tube. The presence of sesame is always distinctly indicated by the rose or red coloration of the acid solution; other oils leave the acid colorless or communicate to it a slightly yellowish tinge.

This reaction is extremely delicate and permits the sure recognition of the presence of one per cent. of sesame oil not only in olive oil but in all fatty mixtures as well as in soap.

This process was presented before the Academy of Sciences by M. Debray, February 20, 1888, and was awarded the gold medal of the Société d'Encouragement. (Report of M. Muntz, in the name of the Agricultural Committee, February 20, 1889.)

Examination for Cotton-seed Oil.—Until recently, the detection of cotton-seed in olive oil was considered impossible, and accordingly, the different scientific societies and several chambers of commerce promised great prizes to the inventor of a process which would detect this adulterant.

Two methods were proposed simultaneously—one by M. Bechi, the other by myself. These two proccesses, which at first sight appear quite analogous and based upon the same reaction, differ completely from the scientific standpoint as well as in the exactness of the results obtained. M. Bechi has based his process upon the direct action of silver nitrate upon the oils. As long ago as 1878, we made some experiments with M. Puget of a similar nature, and the uncertainty of the reactions led us to abandon them entirely.

M. Bechi's process possesses the serious inconvenience of causing us at times to reject as adulterated, oils which are absolutely pure, and thus work injustice and create a considerable prejudice against the firms which have sold them. From results obtained at the Institut National Agronomique of Paris, as well as in other laborotaries, a deep coloration has been found with oils absolutely pure. Outside of these inconveniences, which are sufficient to cause us to throw it aside, it has a defect of being based upon a coloration having no well-defined chemical character, and it produces effects with different substances, the action of which it is impossible to explain. The use of colza oil has the serious fault of bringing into the reaction a second oil which may be impure and completely vitiate the results. Finally, the conclusions reached by the Italian scientific commission, instituted at Rome by act of the ministry to study the Bechi process, show that it is not certain on quantities of less than fifteen per cent. It solves the problem of finding less than ten per cent. no better than the Cailletet process, which shows the presence of fifteen per cent. The same commission declared also that olive oil containing glycerin, free fatty acid, formic acid, acetic acids, does not give a sure reaction with the Bechi reagent. Now, since all olive oils contain free fatty acid from several tenths of one per cent. for virgin oil to 100 per cent. in some industrial oils, what conclusions can we reach?

The Bechi process will give, from fifteen per cent. up, a brown coloration of variable intensity, but in oil containing cotton-seed oil, which is fresh and well refined, the only sort used for edible purposes, we have a very weak reaction; while with an olive oil perfectly pure, but containing organic or mineral matters in suspension or solution, which have an action upon the reagents, we should have a pronounced coloration.

That is why I gave up these uncertain and variable results obtained in 1878 and studied the action of the nitrate of silver not upon the oil itself but upon the products of saponification derived from it. The results obtained exceeded my expectations, and have been published by the press as the Milliau process.

Mailliau Process, Mode of Procedure.—In a porcelain dish of 250 cubic centimeters capacity, fifteen cubic centimeters of the oil to be investigated are heated to about 110°, then there is slowly poured on the oil a mixture of ten cubic centimeters of a solution of caustic soda of 36° B., and ten cubic centimeters of alcohol of 90° B. When the mass boils it becomes clear and homogeneous; 150 cubic centimeters of hot distilled water is added and boiling continued to expel the alcohol. The fatty acids are displaced with ten per cent. sulfuric acid solution added in slight excess, and the pasty acids immediately collected with a small platinum spoon. They are washed by shaking several times in a test tube with an equal volume of cold distilled water. The drops of water are drained off and they are then poured in a tube 2·5 centimeters in diameter and 9 centimeters long; fifteen cubic centimeters of alcohol ninety-five per cent. and two cubic centimeters of three per cent. nitrate of silver solution are added. The tube is protected from the light in the water-bath at 90° C. until about one-third of the alcohol is expelled, which is replaced by ten cubic centimeters distilled water. The heating is continued a few minutes and the coloration of the insoluble fatty acids is observed. *The presence of cotton-seed oil in any proportion whatever causes a mirror-like precipitate of metallic silver, which blackens the fatty acids of the mixture.*

The members of the Agricultural Committee, composed of the greatest savants of France, MM. Pasteur, Eug. Tisserand, Boitel, Chatin, Heuge, Hardi, Rissler, Schloesing, Ronna, Lavaland, Muntz, Prillieux, Maret, Hon. Baron Thenard, Liebaut, after having tested the process on 128 samples from different provinces have had the kindness to confer upon me the gold medal for this method of analysis, and I will take the liberty to present the conclusions of their Secretary, M. Muntz, director of the laboratories de l'Institut National Agronomique: "The preliminary saponification applied to the examination of fatty matters constitutes a new method on which we can confidently rely, not only in the analyses of edible products but besides of those used for industrial purposes and also for soaps." (February, 1889.)

Before proceeding with this monograph, it is, of course, well understood that the same processes can be used for the detection of peanut, sesame and cotton-seed oils, in all other fatty mixtures.

Peanut Oil.—Peanut oil, apart from the arachidic acid which it contains, presents no special characters, as you can observe by examination of the chart upon which are indicated its physical and chemical properties.

Sesame Oil.—The purity of sesame oil may be demonstrated by shaking ten cubic centimeters of oil, first with five drops of sulfuric acid of 53° B., then with five drops of nitric acid of 28° B. The oil undergoes a progressive change of color through various shades from light green to red. The final red coloring matter obtained by this oxidation process turns yellow by the action of alkalies and returns to its original color with acids. This curious phenomenon does not take place with other oils but is obtained sometimes when working on sesame oils slightly adulterated; besides the industrial oils from hot pressing, though pure, may give negative results. I have devised a rapid process, especially applicable for the recognition of castor oil in the industrial sesame oils.

Mailliau Process.—For the rapid identification of castor oil and sesame, ten grams of the oil are shaken up with four drops of sulfuric acid of 66° B., a drop of nitric acid of 40° is added and shaken violently. Pure sesame oil blackens immediately, while that containing castor oil remains turbid yellow.

Cotton-seed Oil.—Concerning this oil, from a chemical standpoint, we have nothing particular to say. From the industrial point of view we may state that this product becomes more useful every day. Its cheapness allows everybody to use it, and this fatty material daily augments its important place in the markets of the world.

We will pass rapidly over the drying oils, poppy seed, linseed, walnut, cameline, over those of the cruciferæ, colza, rape and mustard, as well as the oils of the sweet almond, hazel nut and castor, the properties of which are shown upon the chart.

I will take the liberty, however, of mentioning a rapid process which I have devised for detecting the presence of castor oil in other oils. It is well known that the oils in general are soluble in petroleum ether, while castor oil, which distinguishes itself by its solubility in alcohol, is likewise remarkable for its insolubility in petroleum ether. Unfortunately this insolubility disappears at the ordinary temperature when a soluble oil is adulterated with a small proportion of castor oil.

It is only necessary to demonstrate its insolubility by shaking in a test tube one volume of the oil to be examined with two volumes of petroleum ether, and cooling the mixture to — 16° C. At the end of a few minutes the mass coagulates, and the oil separates if castor oil is present, while the liquid remains homogeneous if it is pure. This phenomenon is especially curious because it will be noted that the freezing point of castor oil unmixed with petroleum ether is much lower than that of most other oils.

SOLID VEGETABLE OILS.

Cocoanut and Palm Nut Oils.—The production of these oils, which is continually increasing on account of their extensive use in the manufacture of soap during the last few years, has been made the object of several adulterations. Independently of the general chemical and physical character of these oils, as well as the sulfuric saponification which I have mentioned, we can employ with good results the determination of the saturation equivalent with normal caustic soda solution.

These oils, containing a greater amount of the lower fatty acids, require for their saturation a larger quantity of sodium oxide. To recognize these oils, it is only necessary to determine the number of cubic centimeters of normal solution required for the saturation of five grams of the pure fatty acid, viz: cocoanut oil, 24·1; palm nut oil, 22·5; while the average of the other liquid oils is seventeen to eighteen cubic centimeters only. This process presents some inconveniences, especially when trying to discover adulteration in small quantities, because it must be noted that the adulteration of these oils is practised only within certain limits, otherwise their appearance would lead to its detection. Besides, when an oil is made from old or spoiled seeds, the saturation is a little less.

Since the detection of adulterations in these oils depends on variations of a few tenths of a centimeter which might be caused by variations in quality of the oils themselves, or the method of operating, it is necessary to be very circumspect in the use of this truly scientific process.

With palm nut oil this error might be greater because it is customary to balance the low saturation of the seed oils by the addition of cocoanut oil. As, for example, five grams of fatty acids from a mixture containing forty-five per cent. of palm nut oil, forty-five per cent. cocoanut oil and ten per cent. peanut oil, require precisely 22·5 cubic centimeters normal solution for their saturation.

Iodin Number.—This determination is very useful because these oils, being very rich in saturated acids, absorb much smaller quantities of iodin than most other oils. For example, peanut gives ninety-seven; while cocoanut and palm nut show only nine to sixteen. Unfortunately, this difference of seven between the maximum and minimum.

throws us out of the way for small quantities of admixture, so much so that different authors fail to agree upon the average variation; some giving eight to nine only, while we are accustomed to find from thirteen to fifteen.

To recapitulate, this process, which if it gave constant results would be excellent, fails to give sufficiently accurate indications to detect adulteration of cocoanut oil when in small proportions. It is worse with palm nut oil and of no value to distinguish between the two.

Continuing our investigations in another direction we have fortunately found a process which gives constant results when used upon these oils after a preliminary neutralization.

We have discovered that cocoanut and palm nut oils are entirely soluble in absolute alcohol. At a temperature of 30° to 31° C., the former requires two volumes, and the latter four volumes, for complete solution.

It is a curious phenomenon that the smallest addition of vegetable or animal oils destroys this solubility in the same quantities of absolute alcohol. The solubility of the mixture is not proportional to its composition, but the mixture acts entirely like a distinct body.

Mode of Procedure.—First operation: Twenty cubic centimeters of the oil are shaken in a test tube with forty cubic centimeters of ninety-five per cent. alcohol. This indispensable preliminary treatment may give certain indications. Oil, soluble in ninety-five cent. alcohol, castor and rosin oil, etc., are thus discovered, while mowrah and karite oils give a milky turbidity to the alcoholic stratum.

Second operation: Five cubic centimeters of the neutralized cocoanut oil are measured with a pipette into a graduated test tube and ten cubic centimetres absolute alcohol added. The temperature is raised to 31°, the tube shaken violently for half a minute and then immersed in a water bath, kept at a temperature slightly above that of the tube.

Pure cocoanut oil dissolves completely and the solution remains clear. Any addition of another fatty matter causes precipitation; the material in solution being in a state of molecular equilibrium, which is destroyed by the slightest modification.

Cocoanut oil containing palm nut oil precipitates when the proportion of the mixture amounts to twenty per cent.; below this the mass remains turbid.

The verification of palm nut oil is made in the same manner, only using twenty cubic centimeters absolute alcohol instead of ten, temperature remaining the same, 30° to 31°. Five cubic centimeters of palm nut oil containing twenty per cent. or more of cocoanut oil, dissolves in fifteen cubic centimeters of absolute alcohol. In the same proportions pure oil does not dissolve, and the mixture remains turbid.

A mixture of cocoanut, palm nut and peanut oils, in such proportions that the oil would appear pure by the indices of saturation, would easily be discovered by this process.

If we work at a lower temperature, the proportion of absolute alcohol must be increased. For example, at 25° to 26° it is necessary to double the quantity; for five cubic centimeters of cocoanut oil, use twenty cubic centimeters of alcohol, and for the palm nut forty cubic centimeters.

The same method may be used to determine the purity of cocoanut and palm nut cakes by first extracting the oil by means of a solvent and then operating on it in the manner described.

This process, which I have had the honor to describe, when carefully executed, enables us to determine in a few minutes adulterations of these oils which might cause bad results in soap making, which employs hundreds of millions of kilograms per annum, and in agriculture, which uses the cakes for cattle food. This process was presented to the Academy of Sciences, October 12, 1892, by M. L. Troost, and has been the subject of a favorable report to the Minister of Agriculture.

Let us pass rapidly over palm oil, of which the principal chemical properties are not remarkable except its partial solubility in absolute alcohol which is ten per cent. Also we will pass over the mowrah, which, as I have already mentioned, is identified by the milky white turbidity which it communicates to alcohol by shaking.

Illepi Oil.—This product, the titer of which is 52°·5, and cotton-seed margarine, or stearine as it is called here, whose chemical reactions are the same as the oil itself, will not long detain us.

While closing the description of the solid vegetable oils, I wish to mention karite oil, which comes from the French province, Soudan, which I have been especially directed to investigate by the Chamber of Commerce of Paris, and the Chamber of the syndicate for the manufacture of soap and candles.

It was very important for us to know how to utilize the great forest which covers the largest part of French Soudan. It is composed chiefly of the wild acacia and the karite or butter tree. The natives collect the nuts which fall from the trees, crush the kernels, treat the pasty mass with boiling water, and skim off the fat which comes to the surface. This fat, which is solid at the ordinary temperature, is used as an edible butter.

Without speaking about the great uses to civilization of this product, I must mention its remarkable chemical properties. The fatty acids, having a titer of 52°·5 C. combine with soda to produce an extremely hard soap. For candle making they would probably give better results, after preliminary treatment to remove the resinoid matters which they contain and which hinder the crystallization of the fatty acids.

The presence of these resins lowers the saturation to 14·9, and, like the mowrah, this oil causes turbidity by shaking with alcohol. (Communication of M. Mailliau to the Société d'Encouragement of Paris in 1892.)

SOLID ANIMAL FATS.

These are colored brown by a stream of chlorine gas.

Butter.—The analysis of this material, which has attracted so much attention during the last few years, is not so difficult as some imagine, but requires the skill of a practical and experienced analyst. The specific gravity of butter is notably lower than that of tallow and lard. It is the same with the iodin number and the freezing point of the neutral fat. The saponification and the solubility in absolute alcohol on the contrary are notably higher.

We can further confirm our results by microscopical examinations; melted butters showing under the microscope a collection of small regular spheres. Adulterated butter shows, on the contrary, abnormal figures, as well as crystals, which appear brilliant in the dark field of the polarizer.

By determining the fixed and volatile fatty acids, and the point of solubility in alcoholic toluene, a skilled analyst familiar with these processes can easily determine admixtures above ten per cent. Below this point, I do not believe any adulteration would be profitable. Natural butter contains about eleven per cent. soluble and volatile fatty acids and eighty-seven per cent. fixed fatty acids. Besides, alcoholic toluene dissolves it almost entirely.

Tallow.—The properties of tallow are so well known that they require no description. The distinction between beef and mutton tallow is a matter of interest and presents great difficulties from the chemical standpoint, and we can observe differences only by taking the melting and solidifying points of the neutral fat and those of the fatty acids.

Lard.—Lard adulterated with cotton-seed oil is easily tested with nitrate of silver. If the lard has been altered by time or by other causes, it is necessary before using this reagent upon the fatty acids, to take the precaution of purifying the fat in the manner in which I have indicated at the beginning of this lecture. We will thus avoid the slight reduction which is produced by decomposition products.

Some authors strongly believe in the use of the iodin number, which will give good results in the case of large admixtures, as well as for quantitative analysis of such a mixture. But it is quite illusory for the detection of a small proportion of cotton-seed oil, for we must consider that the iodin number of pure lard varies within considerable limits, and it would be possible to correct for the high iodine number of cotton-seed oil by the addition of tallow, which will lower it appreciably. In such a mixture the action of nitrate of silver on the fatty acids enables us to discover adulteration even below five per cent.

Tallow is detected by observing, under the microscope, the crystallization of the fat from ethereal solution.

VARIOUS OILS.

The following oils, which frequently are used for the adulteration of agricultural fatty materials, are easily detected:

Fish Oil:—by its iodin number, its solubility in absolute alcohol, the presence of cholesterin, and finally the brown coloration by chlorin, and red by caustic soda and phosphoric acid.

Resins:—by their density, their saturation, their solubility in absolute alcohol, and the deviation of the plane of polarization. Besides, it is easy to isolate them because the majority of compounds which they form with metallic salts are soluble in ether while those of the fatty acids are insoluble.

Resin Oils:—by their property of not saponifying with caustic soda, by their insolubility in glacial acetic acid, and by the characteristic purple coloration which they give with fuming stannic chloride.

Olein Oil of Commerce:—by its solubility in alcohol and by its specific gravity.

Finally, the mineral oils:—by their iodin numbers, their indifference to the action of caustic soda, and their insolubility in absolute alcohol at 15° C.

Gentlemen, we have nearly finished all we have to say in our lecture. The processes which we have just enumerated are applicable indiscriminately to fatty matters, both edible and industrial, for the determination of their purity, with an approximation sufficient for the majority of cases. The results obtained will be more conclusive if they are compared with those from products of the same origin and known purity. Banish the thought that in this short discourse we have wished to indicate in an absolute manner those processes which must be used and those which should be rejected. We have desired only to explain the methods which have given us the best results in the thousands of analyses which we have had occasion to make on fatty materials, including 50,000 for olive oil alone.

Although most of the processes which I have just indicated were devised and perfected in our laboratory, and have been adopted by several governments, I have not, however, the presumption to feel that we have definitely finished this question. I consider, on the contrary, that in the vast unexplored region of the fatty series, we have only taken a few steps; but I feel at the same time that we are now in the possession of sensitive and scientific methods which permit us to detect mixtures, the determination of which has appeared impossible up to the last few years.

The mission with which I have been charged by the French and Tunisian Governments in the interests of commerce and industry, shows you to what extent these countries are desirous of facilitating the exportation of pure and satisfactory products. France furnishes the best growth of virgin olive oil, from Aix en Provence and Nice. Tunis, also, furnishes, but at a less price, olive oils of excellent quality, which we can certify without analysis, because the Government imposes such heavy export and import duties upon seed and seed oils that it would be impossible to practise the smallest amount of sophistication.

Those who deal in olive oils often make the remark that pure oil is too strong and that it is improved in flavor by a mixture with seed oil. Without discussing this inexact statement, I believe that it would be preferable in every instance for the dealer to buy pure olive oil and to make his own mixtures. He would thus profit by the difference in price, which averages about sixty francs per 100 kilograms.

I hope you will pardon the dryness of the subject which we have just discussed, in considering how important it is for our two countries to have the same means of making analyses of American and French products. When we arrive at a complete understanding, discussions and reclamations will become impossible, and I cannot better conclude than by expressing the sincere wish that its realization will permit the two republics to bind more closely together their commercial relations.

Thanks, gentlemen, for your kind attention.

A GENERAL COMPARATIVE TABLE FOR THE ANALYSIS OF FATTY MATTER.

		FATTY SUBSTANCE.	1 Density at 15° C.	2 Action of Nitrous Vapors.	3 SULFURIC SAPONIFICATION. Absolute.	 Relative.	4 INDICES. Bromin.	 Iodin.	 Acetyl.	5 Freezing Points of Oils.	6 Fusing Points of Fatty Acids.	7 Solidification of Fatty Acids.	8 Saturation by Na_2O. Number of Cubic Centimeters of Normal Liquid Absorbed by Five grs. of Fatty Acid.	9 Solubility in Absolute Alcohol. Number of Grams of Neutral Oil Dissolved by 1,000 Grams Alcohol.	10 Deviation of the Plane of Polarization.	CHARACTERISTIC PROPERTIES.
1	Liquid Vegetable Oils.	Olive,	0·915 to 0·917	Solidification. Elaidin melts at 32°	35°	94°	500 to 544	80 to 84	4·7	+ 1 to 4°	27°	23°	17 86	43	0·6 Sacchar.	1. *Action of Nitrous Vapors.*—Operate by Poutet's process, pouring on twenty grams oil one gram H_2SO_4 and one gram HNO_3. The characteristic colorations are first with H_2SO_4 green, [illegible] with H_2SO_4 + HNO_3 grey, green; then after [illegible] straw-yellow. [illegible] setting in hard mass, color of white butter.
2		Peanut,	Unshelled, 917·5 Shelled, 921	Liquid Mass.	46°	127°	530	97	3·5	— 1°	31°	28°	17·82	66	Variable.	2. Arachidic acid, $C_{22}H_{44}O_2$ (fusing point [illegible]), is characteristic and allows the detection of peanut oil in its [illegible].
3		Sesame,	923	"	54°	150°	695	104	3·4	— 5°	26°	22°	17·70	41	"	3. *Milliau's Process.*—The red color obtained by treating the purified fatty acid of the oil with hydrochloric acid and sugar is characteristic. The fatty acid is first [illegible] and tested [illegible].
4		Cotton-seed (edible),	922	"	52°	144°	645	108	15·3	— 12°	36° to 37°·5	35°	18·17	62	"	4. *Milliau's Process.*—The black color obtained by the reduction of $AgNO_3$ in the presence of the saponified products of the purified oil is characteristic.
5		Poppy (drying),	925	"	80°	222°	835	133	13·1	— 18°	20°·5	16°	18·13	45	— 0·7°	5. Poppy oil when used as an adulterant of olive oil, prevents the solidification of the mass by the action of nitrous vapors.
6		Colza,	914·5	"	48°	133°	640	99	6·3	— 6°·5	17°	16°	16·49	20	Variable.	6. A solution of potassium hydroxid treated with saponified colza oil blackens with lead acetate, and reddens with potassium nitroferricyanid.
7		Rape seed,	915	"	56°	155°	632	103	5·9	— 4°	15°·5	15°	16·68	15	+ 15°	7. Density and fusing points of the fatty acids.
8		Linseed,	932·5	"	121°	336°	1,000	156	8·7	— 27°·5	23°	21°	17·98	70	Inactive.	8. Density, freezing point, sulfuric saponification and iodin index.
9		Walnut,	926	"	99°	275°	737	144	7·3	— 30°	Fluid.	Fluid.	18·26	44	"	9. Sulfuric saponification, iodin index, freezing points and fluidity of the fatty acid.
10		Cameline,	926	"	51°	141°	817	132	7·5	— 18°	"	"	17·90	78	— 3	10. Iodin index, freezing point and fluidity of the fatty acid.
11		Beechnut,	921	"	59°	163°	652	106	6·1	— 18°	24°	17°	18·18	45	Almost Inactive.	11. *Brullé's Reagent.*—Two cubic centimeters nitric acid, [illegible] grams dried albumen, ten cubic centimeters oil: when agitated the mixture takes a characteristic vermilion tint.
12		Mustard seed,	918	"	39°	108°	763	96	6·9	— 5° to 0°	16°	15°	17·97	28	+ 3	12. Sulfuric saponification and iodin index.
13		Sweet almond,	918·5	Soft Consistence.	47°	130°	644	98	5·7	— 10°	14°	5°	18·22	39	Almost Inactive.	13. Nitrous vapors and solidification of fatty acid.
14		Hazelnut,	917	Rather Firm.	31°	86°	561	87·5	4·9	— 21°	25°	23°	17·63	33	"	14. Sulfuric saponification and freezing points.
15		Castor,	965	Formation of Ricin-Elaidin.	40°	111°	559	84	15·3	— 18°	12°	4°	16·77	Soluble.	Mean = 43	15. Density, solubility in alcohol and crystallizable acetic acid, insolubility in petroleum ether, deviation of the plane of polarization.
16	Solid Vegetable Fats.	Coprah,	924·5	Solidification.	17° 5	48° 5	74	12	—	Solid 22°·5 Fusion 26°	26°·5	22°·7	24·1	Solub'e at 31° C. in 2 vol. alcohol.	Undetermined.	16. *Milliau's Process.*—The neutralized oil is soluble at 31° in twice its volume of absolute alcohol, and becomes insoluble on the addition of seed oils. Saturation, iodin index.
17		Cabbage palm,	922	"	19°	52°·7	99	16	—	23°·5 26°·5	27°	24	22·5	Soluble at 31° C in 4 vol alcohol.		17. *Milliau's Process.*—Like the preceding, but requires four volumes of absolute alcohol.
18		Palm,	915	"	17°	47°	315	51	—	25° to 35° 33° to 39°	46° to 47°	42° to 46°	18·5	400		18. Density, sulfuric saponification, partial solubility in absolute alcohol.
19		Mowrah,	915	"	26°	71°	404	65·3	—	23° 27°	46°	42° 5	15·5	160		19. Density, saturation, when shaken with alcohol gives a characteristic milky tint.
20		Margarin from cotton-seed oil,	920	Soft Consistence.	47°·5	136°	588	84	—	14° 28°·3	46°	42° 5	18·2	61		20. Iodin index, solidification of the oil; Milliau's Process (4).
21		Illipi,	917·5	Solidification.	13°·5	37°	152	24·7	—	26° 39°	56°	52°·5	17·7	260		21. Sulfuric saponification, iodin index, fusing point of the fatty acids.
22		Karite,	917·7	"	28°·5	79°	416	67·2	—	23° 25°·5	56°·5	52°·5	14·9	80		22. Fusing point of the fatty acids, saturation, when agitated with alcohol gives a characteristic milky tint.
23	Solid Animal Fats.	Butter,	920 to 936	Solidification.	Mean, 23°	Mean, 63°	160 to 216	26 to 35	—	19° to 31° 21° to 32°	37° to 39°	35° to 37°	21·15	65·4		23. Volatile fatty acids, iodin index, solidification of the neutral matter, saturation, microscopic examination. Are colored brown by a current of chlorine.
24		Suet,	Mutton, 917 Beef, 915	"	16°	44°	247	40	—	33° to 6° 42° to 46° 33° to 35° 38° to 43°	40° to 50° 40° to 48°	45° to 47° 43° to 45°	18·5 18·25	3·18		24. Sulfuric saponification, solidification of the fatty acids, insolubility in absolute alcohol.
25		Lard,	920	"	33°	91°	365	59	—	32° 34°	35°	34°	18·12	43		25. Sulfuric saponification, iodin index.
26	Miscellaneous.	Fish oil,	923 to 930	Liquid Mass.	50° to 100°	138° to 277°	761 to 872	123 to 141	—	Congeals at 0°	—	—	17·71	Cod Liver, 240		26. Iodin index, solubility in alcohol (milky emulsion), fusion point of cholesterin.
27		Rosin,	1·08	—	—	—	718	116	—	—	—	—	15·13	Soluble.	Mean = — 15°	27. Density, saturation, solubility in alcohol, deviation of the plane of polarization.
28		Rosin oil,	960 to 990	Fluid Mass.	—	—	297	48	—	—	—	—	—	Almost Insoluble Cold.	+ 30°	28. Density, deviation of the plane of polarization, insolubility in crystallizable acetic acid.
29		Commercial olein (oleic acid),	900	Solidification. Elaidic Acid.	24°	—	443 to 518	68·5 to 83·5	41 to 63	—	+ 4° to + 12°	0° to + 8°	17·7	Soluble.	—	29. Density, nitrous vapors, solubility in alcohol.
30		Mineral oils,	850 to 930	Liquid.	Petrol., 3° Schist, 22°	8° 61°	80 132	13 21	—	—	—	—	—	Insoluble Cold.	—	30. Density, iodin index, insolubility in alcohol.

[*Proceedings of the stated meeting, held Tuesday, November 21, 1893.*]

HALL OF THE FRANKLIN INSTITUTE,
PHILADELPHIA, November 21, 1893.

WM. H. GREENE, President, in the chair.

The Treasurer called attention to a mistake that had been made in proposing for membership the name of Mr. J. Benjamin Glavin, after that gentleman had already been elected at a previous meeting.

Mr. Pemberton, as a committee of one to prepare a memorial of our late fellow-member, Mr. R. A. Fisher, read his report, which was accepted, with a vote of thanks from the Section. The report is herewith appended to these minutes.

A bill from the Actuary of the Institute for stationery and postage in sending out notices, etc., amounting to $10.99, was approved by the Finance Committee, and referred to the Treasurer for payment. A bill from the Secretary for postage, amounting to $2.60, covering a period of two years, was similarly recommended for payment.

The Actuary was requested to make a draft in favor of R. Friedländer & Son, for 173·25 marks, to cover subscriptions to current journals now due.

The nomination of officers for the year 1894 was then taken up. For President, Prof. E. F. Smith and Dr. Wm. H. Greene were nominated, but Dr. Greene declined the honor of a second term of office, thus leaving Professor Smith the only nominee.

Mr. H. Pemberton, Jr., and Dr. L. B. Hall were nominated for Vice-Presidents, and, on motion, it was voted that nominations for Vice-Presidents be closed.

The recent incumbents of the offices of Secretary, Treasurer and Conservator were re-nominated for their several offices, after which in each case it was voted that nominations be closed. Messrs. Hooker, Haines and Boyer were nominated for membership on the Committee of Admissions, the remaining members of this committee to be as usual the President, Secretary, Treasurer and Conservator.

Mr. L. F. Kebler presented a paper, entitled "Notes on the Examination of Beeswax." This paper, which showed much care on the part of the author, both in the experimental work involved and in the review of the literature of the subject, was well received, and was discussed by the President, Dr. Jayne and Mr. Haines. The paper was referred for publication in the *Journal.*

Dr. Terne read a communication from Mr. Williams, of Wilmington, in which the writer stated that he had tried the method proposed by Mr. Pemberton of determining phosphoric acid in fertilizer analysis, and found it entirely satisfactory. Dr. Terne also stated that the method had been used in his own laboratory with excellent results. Dr. Terne then read an exceedingly interesting paper on "The Availability of Nitrogen in Mixed Fertilizers." This was discussed by the President, Mr. Pemberton, Dr. Jayne and Mr. Haines, and was referred for publication.

The Section then adjourned. WM. C. DAY, *Secretary.*

THE ATOMIC WEIGHT OF MOLYBDENUM.

BY EDGAR F. SMITH AND PHILIP MAAS.

[*Reaa before the Chemical Section of the Franklin Institute, September 19, 1893.*]

The present atomic value assigned this element is based upon the results obtained by Dumas (*Ann. Chem. Pharm.*, **105**, 84, and **113**, 23), Debray (*Compt. rend.*, **66**, 734) and Lothar Meyer (*Ann. Chem. Pharm.*, **169**, 365). The method pursued by Dumas consisted in the reduction of molybdenum trioxide. Debray also adopted this procedure, but in addition made several experiments upon the precipitation of the trioxide in an ammoniacal solution by silver nitrate. Lothar Meyer's value (95·9) is deduced from results obtained by Liechti and Kemp (*Annalen*, **169**, 344) in their analyses of the chlorides, $MoCl_2$, $MoCl_3$, $MoCl_4$ and $MoCl_5$. The chlorine in each was determined as silver chloride and the molybdenum as disulphide. Clarke (*A Recalculation of the Atomic Weights*, Washington, 1882) expresses the opinion that the most reliable results are those that have been obtained by the reduction of the trioxide. Of the work of Liechti and Kemp, he remarks: "Traces of oxychlorides may possibly have contaminated the chlorides and augmented their atomic weight." Rammelsberg (*Berichte d. d. Chem., Gesellschaft*, **10**, 1776) made one experiment in the reduction of the trioxide, from which he calculated the atomic weight of molybdenum to be *96·18*.

Thinking that additional light could be thrown upon the magnitude of this constant by proceeding in a different direction, we utilized a reaction first observed by Debray (*Compt. rendus*, **46**, 1098; *Ann. Chem. Pharm.*, **108**, 250), which, in the hands of others (Péchard, *Compt. rend.*, **114**, 173; *Zeit. f. anorg. Chem.*, **1**, 262; Smith and Oberholtzer, *Journ. Am. Chem. Soc.*, **15**, 18, and *Zeit. f. anorg. Chem.*, **4**, 237) has proved to be a most excellent means of determining molybdenum and separating it from its intimate associate—tungsten. We refer to the action of hydrochloric acid gas upon molybdic acid and molybdates, whereby the molybdic acid is volatilized with ease in the form of an hydroxychloride—$MoO_3.2HCl$. Numerous trials have demonstrated that the reaction expressed by the equation—

$$Na_2MoO_4 + 4HCl = 2NaCl + MoO_3.2HCl + H_2O$$

is quantitative. We exposed pure anhydrous sodium molybdate (at 150–200°) to the action of hydrochloric acid gas, volatilized the molybdenum, trioxide and from the weight of the residual sodium chloride calculated the atomic weight of molybdenum.

The sodium molybdate employed by us was Merck's purest preparation. We recrystallized it many times and then by a careful examination satisfied ourselves that it did not contain silica, sulphates, tungstates or alkaline carbonates—substances that might have been present. The purified salt was dried with extreme care until no further loss in weight was observed. In this anhydrous condition it was preserved in clean weighing bottles, which were kept in desiccators to exclude dust and moisture. The specific gravity of the anhydrous salt was determined, alcohol being used for the purpose. The value found was 6·9780. The balance employed by us was of the Sartorius design.*

The weights of brass and platinum were of Westphal make and had previously been carefully adjusted for this purpose.

Tared porcelain boats were used to carry the anhydrous sodium molybdate, which was exposed in hard glass tubes to the action of pure and dry hydrochloric acid gas. This was prepared from salt and pure sulphuric acid. The gas as it was evolved was first conducted through a U-tube half-filled with damp silver chloride; it next passed through two flasks containing sulphuric acid, then through a tower of dry calcium chloride and finally through clean cotton, after which it was admitted to the combustion tube where it came in contact with the sodium molybdate. A very gentle heat was applied to the latter and gradually increased to from 150–200° C., beyond which the temperature was not permitted to rise. Moisture was excluded as much as possible. The volatilized $MoO_3.2HCl$ was collected in water. The boats containing the residual sodium chloride were allowed to cool in a slow current of hydrochloric acid gas, then transferred to vacuum desiccators, and the vapor repeatedly exhausted. The weights were taken after the boats had stood one hour. Second weighings were made after the boats had remained overnight in the dry desiccators and showed no appreciable alteration. Barometric pressure and temperature were carefully observed and all weighings reduced to the vacuum standard. Our results are as follows:

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*We would here acknowledge our indebtedness to Dr. John Marshall, of the Medical Department, for the privilege of using this excellent instrument.

Na_2MoO_4 in Grams.	*NaCl in Grams.*	*Atomic Weight of Mo.*
1·14726	0·65087	96 130
0·89920	0·51023	96·094
0·70534	0·40020	96·108
0·70793	0·40182	96·031
1·26347	0·71695	96·087
1·15217	0.65367	96·126
0·90199	0·51188	96 067
0·81692	0·46358	96·077
0·65098	0·36942	96·073
0·80563	0·45717	96 078

Mean, ... = 96·087
Maximum, ... = 96·130
Minimum, ... = 96·031

Difference, ... = ·099

In our calculations we used the following values: Na = 23·05, Cl = 35·45 and O = 16. These have been taken from a revised table of atomic weights, published by Clarke, October, 1891.

The sodium chloride in five of the determinations just given was converted into silver chloride. From the calculated silver contained in the chloride we deduced the atomic value of molybdenum to be 96·10—the mean of five determinations. This figure we regard as confirmatory of the rest of our work.

The sodium chloride which we obtained dissolved readily and to a clear solution in water. Molybdic acid was not found present in it. This was one of the points that we watched very closely, although its presence would have tended to diminish rather than to augment the atomic value found. Another cause of a like result would have been moisture absorbed by the sodium chloride. Against this source of error we likewise took every precaution, and consequently feel that the result *96·08* obtained by us approaches very closely to the true atomic magnitude of molybdenum.

UNIVERSITY OF PENNSYLVANIA, September 16, 1893

[*Proceedings of the stated meeting held Tuesday, December 19, 1893.*]

HALL OF THE FRANKLIN INSTITUTE,
PHILADELPHIA, December 19, 1893

DR. WM. H. GREENE, President, in the chair.

Mr. Boyer proposed for membership the name of Dr. Nelson B. Mayer, 945 North Eighth Street, Philadelphia; the name was referred to the Committee on Admissions.

The Secretary read his annual report which was accepted. The Treasurer also made his annual report, showing cash on hand at the beginning of the year $74.16; receipts during the year, $141; expenditures, $187.64; leaving a balance of $27.52 in the treasury. The Finance Committee audited the Treasurer's account and found it correct.

The Conservator reported that he had on hand a number of volumes of the proceedings of the Section, which, following instructions from the Section, he would dispose of in accordance with his judgment of the best interests of the Section.

Owing to the fact that Prof. E. F. Smith had declined the nomination for President of the Section, on motion it was voted that nominations for President be re-opened.

Dr. D. K. Tuttle and Dr. H. F. Keller were then nominated; the latter gentleman, however, declined, thus leaving Dr. Tuttle the only nominee, when it was voted that nominations be closed. The Secretary was directed to cast the vote of the Section for the following candidates, who were thereupon declared elected to their respective offices:

President, ...	Dr. D. K. Tuttle.
Vice-Presidents, ...	Mr. H Pemberton, Jr. Dr. L. B. Hall.
Secretary, ...	Dr. Wm. C. Day.
Treasurer, ...	Dr. H. W. Jayne.
Conservator, ...	Dr. Wm. H. Wahl.

The Secretary was then instructed to cast the ballot of the Section for Dr. S. C. Hooker, Mr. Reuben Haines, and Mr. C. S. Boyer, as members of the Committee on Admissions, to act with the President, Secretary, Treasurer and Conservator as the remaining four members; the candidates were declared elected.

On motion, it was voted that the Secretary notify the Institute to renew the yearly subscriptions to the current journals subscribed for during 1893.

Dr. W. J. Williams submitted for publication a paper embodying the results of his examination of Pemberton's method of phosphoric acid determination. The main points of this paper had already been brought before the Section at the November meeting by Dr. Terne, who read at that time a communication from Dr. Williams. The paper was referred for publication.

Dr. Bruno Terne then read a paper, entitled "Contribution to Pemberton's Volumetric Method for Phosphoric Acid Determination." This paper was the joint production of Dr. Terne and Mr. Francis Bergami.

Mr. Bergami then followed with a contribution, entitled "Comparison of Pemberton's Method of Phosphoric Acid Determination with the Official Method."

Both papers evoked interesting discussion and comment from many of the members present.

Mr. Reuben Haines was prevented by illness from being present to read the two papers from him announced on the program of the meeting. One of them was presented, namely, "Normal Chlorine in Spring Water near Philadelphia." Owing to the lateness of the hour this paper was read by title and referred for publication. The meeting then adjourned.

WM. C. DAY, *Secretary.*

ROBERT A. FISHER.

Robert Andrews Fisher, a member of the Philadelphia family of that name, died quite suddenly on October 6, 1893. He was the son of Jabez M. Fisher and Nancy Andrews, his wife; having been born on December 21, 1832. Miers Fisher, his grandfather, was a distinguished Quaker lawyer of Revolutionary times.

Mr. Fisher was, in the early fifties, the assistant to Prof. John A. Porter, of Yale College, and, at one time, was Professor of Chemistry at Brown University, which conferred upon him an honorary degree. In those days no facilities were offered in this country, to chemists who were desirous of pursuing advanced courses in their science. He, accordingly, went to Europe, studying at Göttingen and at Heidelberg, and, later on, attending lectures in Paris. Upon his return to America, he accepted the chair of chemistry and mineralogy in the University of California, devoting considerable attention, also, to the mining industry then just developing in the far West. In this direction, in connection with Prof. Samuel W. Johnson, now of New Haven, Conn., his services, as mining expert, were called upon by the Directors of the Richmond mine in Nevada.

During the last fifteen years of his life he was the consulting chemist to several large industrial works in Philadelphia, having been associated with the Pennsylvania Salt Manufacturing Company, in this capacity, during the greater part of this time. The President of this company bears the following testimony to his professional ability:

"Professor Fisher had achieved a high position in his chosen profession of chemistry, having given especial attention to the scientific branch of the art of paper-making, and was considered an authority on all technical and practical questions arising in that particular manufacture. His knowledge, however, was general, and extended largely into the chemical composition of food products and manufactures, and, in this direction, his attainments and clear, concise conclusions rendered his opinions much sought after on all mooted points."

He also devoted much attention to the manufacture of sulphate of alumina from beauxite as well as from other materials, and the number of patents taken out by him bears evidence to his ingenuity and industry. He took an active part, moreover, in the introduction of the sulphite process of paper-making, in the Western States.

Mr. Fisher was a member of the Chemical Section of the Franklin Institute, and also of the American Chemical Society. He was well informed on all the recent advances in his science, particularly in such as relate to the application of chemistry to the industrial arts, and while possessing a keen insight into the important points of many scientific questions, was careful and conservative in his judgment.

Personally, Mr. Fisher was most considerate and courteous in his bearing. He was widely connected in Philadelphia, and endeared himself to many friends. P.

NOTES ON THE EXAMINATION OF BEESWAX.

By Lyman F. Kebler.

[*Read at the stated meeting of the Chemical Section, held Nov. 21, 1893.*]

When the contribution,* entitled "An Examination of Beeswax," by E. G. Parry and P. A. Estcourt, appeared, describing the sophistication of this article in the English market, the writer had nearly completed a communication on the same subject with reference to this country.

The waxes examined, and the results submitted below, were samples sent to this laboratory for the past year from various parts of the country as specimens representing the waxes the dealers had in stock, and it is not more than fair to suppose that the samples submitted for examination were equal, if not superior, to the beeswax in our market.

At first the process of the legally recognized authority was used. After some time a sample which had been rejected was investigated and reported as complying *in toto* with the requirements of the above authority. The writer was ignorant of the rejection of the wax until he had made his report. The wax had been rejected because it was unfit for electrotyping, and must therefore contain an adulterant of some kind, probably "grease" or some fatty substance. The wax was again looked into with the same results. It has since been found by experiment that the impurity could have been detected by using a twenty per cent. solution of sodium hydroxide in place of a fifteen per cent. solution.

The wax was now examined rigidly by the best methods.

In view of the fact that the literature on wax analysis is at best fragmentary and the methods imperfect, and that the object of this contribution is not only to present the condition of wax in our market, but also to make the paper of practical value to analysts, it is desirable to give here a

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* Read before the Brit. Pharm. Conference, Nottingham, through the *Am. Drug. and Pharm. Record*, **23**, 158.

résumé of the best methods employed and the references in the literature.

First, let us consider briefly the composition of beeswax. It is a mixture of *myricin*, *cerin* and *cerolein.*

Myricin ($C_{46}H_{92}O_2$), forms the chief constituent of wax. It is insoluble in alcohol and fuses at 64° C.

Cerolein constitutes only from four to five per cent. of the wax, has an acid reaction, and is the constituent to which wax owes its tenacity, odor and color.

Cerotic acid, or cerin ($C_{27}H_{54}O_2$), is not a constant constituent of beeswax.

B. C. Brodie,* in his classic *Untersuchung über die chemische Natur des Wachses*, has shown that cerin consists essentially of a high fatty acid, *i. e.*, cerotic acid, while myricin is the palmetic ether of melissic alcohol. F. Schwalb † and F. Nafzger ‡ have shown that wax contains small quantities of acids related to cerotic acid, as melissic acid; also some non-saturated acids of the oleic acid series and some alcohols related to cerylic alcohol, as melissic alcohol. They have also proven it to contain saturated hydrocarbons, such as hentriacontane ($C_{31}H_{64}$) and hyptacosane ($C_{27}H_{50}$).

It was thirty-four years after the composition of beeswax was made known, or the way paved for the introduction of a method, before one was proposed for the examination of this article based on the determination of the free and combined acids, respectively.

The Acid and the Ether Numbers.—These were determined by the well-known method of Hübl§ (not the iodine number), who was the first to apply the method in a practical way. The method is sometimes awarded to Hehner, who translated his results into cerotic acid and palmate of myricle. Hehner || applied the method a few months before Hübl

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* 1848, *Ann. Chem.* (Liebig), **67,** 180; *Phil. Trans.*, London, **136,** 147. 1849, *Ann. Chem.* (Liebig), **71,** 144.

† 1884, *Ann. Chem.* (Liebig), **224,** 225.

‡ 1886, *Ibid.*, **235,** 106.

§ 1883, *Dingl. poly. J.*, **249,** 338.

|| 1883, *Analyst*, **8,** 16.

did, but Becker* was the first to apply the principle of Köttstorfer† to the analysis of beeswax. Hübl's method is recognized as the most elegant, most convenient, as well as the best method for establishing the purity of this article. The method ‡ in detail is: heat three or four grams of the wax with twenty cubic centimetres of neutral ninety-five per cent. alcohol, titrate while hot with a semi-normal alcohol solution of potassium hydroxide and phenolphthalein to estimate the acid number; now add twenty cubic centimetres more of the alkaline solution and saponify by boiling the solution briskly with a reflex condenser for one hour, to insure complete saponification. The excess of alkali is then titrated back with semi-normal hydrochloric acid. The number of milligrams of potassium hydroxide required to saturate the free acids of *one gram* of wax is called the "acid number;" that required to decompose the wax ethers, the "ether number."

The acid number varies from nineteen to twenty-one milligrams, the ether number from seventy-three to seventy-six, while their ratio is from 1 : 3·5 to 1 : 3·8. For complete saponification from ninety-two to ninety-seven milligrams of potassium hydroxide are required. After having secured the acid and the ether numbers the quantity of cerotic acid or its equivalent and myricin are easily calculated. Extreme care must be taken in the titration on account of the extraordinarily high molecular weights of both cerotic acid (410) and myricin (676). One cubic centimetre of normal alkali represents 410 milligrams of cerotic acid and 676 milligrams of myricin, respectively.

Determination of the Alcohols.—Unquestionably the alcohols of beeswax belong to the same series, consequently they possess the same chemical properties. Dumas and Stas described an important reaction of the fatty alcohols, viz: the reaction which they give when heated to a moderate temperature with potassium hydroxide. These alcohols when so treated are converted into the corresponding acid or alkaline salt, and hydrogen is simultaneously disengaged. For example, when melissylic alcohol is distilled with potassium hydroxide the alcohol is decomposed, hydrogen being evolved on the one hand, and potassium melissate formed on the other, recalling a more familiar example where potassium acetate is formed by treating ordinary alcohol in a similar manner. The constituents of wax (not alcohol), are not affected by this treatment, consequently by measuring the volume of hydrogen evolved, from a given weight, the proportion of alcohols can be approximately estimated. C. Hell,* H. Strürcke † and F. Schwalb ‡ applied the above reaction to beeswax long before MM. A. and P. Busine,§ but it was these last two investigators who simplified the apparatus and studied the conditions of success. They proceed as follows: melt two to ten grams of the wax in a porcelain dish, mix with an equal weight of pulverized caustic potash, mix the mass again with three or four times its weight of pulverized caustic potash, then introduce the mixture into a flask and heat on a mercury bath to 250° C. for two hours. The reaction begins at 180° C. The volume of hydrogen evolved by one gram of the wax, varies from 53·5 to 57·5 cubic centimetres at 0° C., and 760 millimetres pressure, corresponding to a percentage of melissic alcohol varying from 52·5 to 56·5.

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* 1880, *Corr. Bl. Ver. anal Chem.*, **2,** 57; Abst., *Zeit. anal. Chem.*, **19,** 241.

† 1879, *Zeit. anal. Chem.*, **18,** 199 and 431; *Analyst*, **4,** 106.

‡ 1892, H. Röttger, *Chem. Ztg.*, **16,** 1837; *J. Chem. Soc.*, **64,** 351. G. Buchner, *Ibid.*, **16,** 1922; *J. Chem. Soc.*, **64,** 351.

Determination of Hydrocarbons.—The hydrocarbons are determined very readily by treating the residuum of the preceding determination with an appropriate solvent, as ether. In the above residue all the acids of the wax and the alcohols have been transformed into a state of alkaline salts, while the hydrocarbons alone remain intact. Hydrocarbons are found in wax in almost constant quantity, varying from 12·72 to 13·78 per cent.

The writer did not execute the last two operations because the apparatus of M. Dupre was not available.

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* 1884, *Ann. Chem.* (Liebig), **223,** 269; *Chem. Ztg.*, **8,** 859.

† 1884, *Ibid.*, **223,** 295; *Chem. Ztg.*, **8,** 860.

‡ 1886, *Ibid.*, **235,** 106.

§ 1890, *Bull. Soc. Chim.* (3), **3,** 567; *Chem. Ztg. Reper.*, **14,** 225.

The Iodine Number.—By treating wax with iodine a new number is obtained which is of considerable value for analytical purposes. This number was determined by the conventional method of Hübl.* The iodine absorbed by the wax being small it was necessary to use a larger quantity of the substance than ordinarily, consequently more chloroform was needed. The method † in detail is: dissolve two grams of the wax in forty cubic centimetres of chloroform in a glass stoppered flask. Add twenty-five cubic centimetres of an iodine solution, containing twenty-five grams of iodine and thirty grams of mercuric chloride dissolved in ninety-five per cent. alcohol and made up to one litre, and shake. Place the flask into a dark closet for three hours, then add fifteen cubic centimetres of a ten per cent. solution of potassium iodide and 100 cubic centimetres of water, finally titrate the free iodine with a standardized solution of sodium thiosulphate. The "iodine number" expresses the per cent. of iodine absorbed by the wax. It is quite essential to carry blank experiments in order to secure reliable results.

The Melting Point.—This is determined as follows: dip the bulb of the thermometer into the sample of melted wax, for an instant. On cooling, the bulb is covered with a film of the wax. Introduce the thermometer into a wide mouth bottle through its perforated cork. The bottle is now hung into a beaker containing water at about 65° C., carefully noting the temperature at the instant a hanging drop is formed; this is taken as the melting point. Other ‡ methods were used but the above method gave concordant results without consuming too much time.

Specific Gravity.§—This was obtained by diluting alcohol so that the wax, previously melted and cooled normally, would float indifferently in it. The specific gravity of the alcohol being identical with that of the floating wax, it is necessary only to secure the specific gravity of the liquid with a picnometer, or a specific gravity spindle, and we have the specific gravity of the wax. The most trustworthy methods employed for securing the specific gravity of fats, waxes, etc., are given in the *U. S. Bull.*, No. **13**, 40-43.

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* 1884, *Dingl. poly. J.*, **253,** 281; *J. Chem. Soc.*, **46,** 1435; *Am. Chem. J.*, **6,** 285; *J. Soc. Chem. Ind.*, **3,** 641.

† *U. S. Bull.*, No. **13,** 818.

‡ 1883, Guichard, *Proc. Royal Soc. Ed.*, **106,** 432, 532; *Zeit. anal. Chem.*, **22,** 70. 1884, H. Krüss, *Zeit. f. Instrumentenkunde*, **4,** 32. 1886, C. Reinhardt, *Zeit. anal. Chem.*, **25,** 11. 1887, H. W. Wiley, *J. anal. Chem.*, **1,** 39.

§ 1879, Hager, *Analyst*, **4,** 206.

Stearin, Stearic Acid, etc.—Any foreign acid can easily be detected by Hübl's method. Fehling's* method gives an unmistakable turbidity with *one per cent.* of stearic acid, and is executed thus: boil one gram of the wax in a test tube with ten cubic centimetres of eighty per cent. alcohol for a few minutes, allow to cool to 18° or 20° C., filter, to the filtrate add water and shake. If stearic acid is present it separates in flocks on the surface, leaving the underlying fluid nearly clear.

A. H. Allen† gives a method depending on the insolubility of lead stearate in alcohol. Proceed thus: boil the wax for forty minutes with twenty parts of alcohol, cool; the cerolein and some of the stearic acid remain in solution. Filter and treat the filtrate with an alcoholic solution of lead acetate. If a flocculent precipitate of lead stearate is formed, stearic acid is contained in the wax.

F. Jean's‡ method was also tried but proved unreliable, at all events waxes proven to be free from stearic acid by Hübl's and Fehling's methods gave unmistakable evidence of stearic acid.

7·8 centimetres of semi-normal alkali equals one gram of commercial stearic acid.

Stearin may be detected by the methods employed for stearic acid.

Rosin.—E. Donath's § method, modified by E. Schmidt,‖ was applied in each case, and is executed thus: place five grams of the wax into a flask, add twenty cubic centimetres of crude nitric acid (specific gravity 1·32), heat the mixture to boiling and keep at this temperature for one minute. Add an equal bulk of cold water, then an excess of ammonia water. With pure wax the alkaline fluid is colored yellow only, but in presence of rosin a deep brown.

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* 1858, *Dingl. poly. J.*, **147,** 222; see, also, *Chem. Ztg.*, 1890, **14,** 606.

† *Commercial Organic Analysis*, **2,** 213.

‡ 1891, *Bull. Soc. Chem.* (3), **5,** 3.

§ 1873, *Dingl. poly. J.*, **205,** 131; abst. *Zeit. anal. Chem.*, **12,** 325.

‖ 1877, *Ber.*, **10,** 131, 837; *Zeit. anal. Chem.*, **17,** 509.

Paraffin.—Paraffin is a common adulterant of beeswax. In fact, some samples of wax might more appropriately be reported as adulterated paraffin, for as high as eighty per cent. of this substance has been found mixed with wax in our markets.

There are many methods[*] for detecting paraffin and its allies, but the process of the United States Pharmacopœia has given the writer results as reliable as any, and is outlined thus: "if five grams of yellow wax be heated in a flask for fifteen minutes with twenty-five cubic centimetres of sulphuric acid to 160° C., and the mixture diluted with water, no wax-like body should separate."

Care, however, must be exercised in applying the test, as has been shown by C. C. Sherrard[†] and C. M. Morse.[‡]

The paraffin is estimated by decomposing a portion of the wax with concentrated boiling sulphuric acid, the charred mass cooled, washed with water, dried and extracted with a Soxhlet's apparatus by means of ether. The paraffin hydrocarbons are thus obtained in a fairly pure state.

Japan Wax.—E. Buri[§] regards this wax as a mixture of glycerides and not as a dipalmatin.

A number of methods are claimed by their various authors to be efficient in detecting this adulterant in beeswax, but none has proven itself very effective in the writer's hands. The borax[‖] and sodium carbonate[¶] methods only deserve mention. Experience has shown that it would be better to abandon the borax method also, or at least to be

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[*] See references *U. S. Bull.*, No. **13,** 828; and *Chem. Ztg.*, 1890, **14,** 607.

[†] 1892, *Proc. Am. Pharm. Assoc.*, **40,** 252.

[‡] 1888, Thesis, College Pharm., Mass.

[§] 1879, *Arch. d. Pharm.* (3), **14,** 403.

[‖] Hager, 1862, *Pharm. Centrhalle*, **3,** 207; 1880, *Dingl. poly. J.*, **238,** 356.

[¶] Donath, 1872, *Dingl. poly. J.*, **205,** 137; *Allen's Com. Org. Anal.*, **2,** 212.

extremely cautious in judging from its results, for the separation into layers takes place easier on paper than in the test tube.

Donath's* general reaction for rosin, tallow, stearic acid and vegetable wax gives a valuable indication but is not specific enough. He directs to boil one or two grams of the wax with six or eight cubic centimetres of a concentrated solution (1 to 6) of sodium carbonate for one minute; if an emulsion ensues, which is persistent after the liquid has cooled, the wax, contains one or more of the above adulterants.

Soap.—This adulterant can easily be detected by boiling a small piece of the wax a few minutes with water, cooling, filtering and treating the filtrate with hydrochloric acid. A precipitate indicates the presence of a soap.

Mineral Matters.—Such substances as *kaolin*, *gypsum*, *heavy spar*, *yellow ochre*, *etc.*, are said to be frequently used as adulterants for beeswax, but examinations of late show that the day of such gross sophistication is nearly past. At the present time, adulteration has in many cases become a science.

Starches.—The various starches can easily be detected with the aid of a microscope or by boiling a small piece of the beeswax with a little water, cooling, filtering and to the filtrate adding a few drops of a test solution of iodine. A blue coloration indicates starch.

Above is given a table embodying the results of the analysis of *sixteen* samples of the wax as received, of which *eight* were pure and *eight* adulterated.

Wax No. 1 is placed at the head as a standard, because it is of known purity and is not to be included in the other sixteen samples.

Neither No. 3 nor No. 9 contained any detectable adulterant, yet the ether number is low. Several trials were made, in both cases, to obtain if possible a higher ether number, but without success. Each sample was boiled for

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* Donath, 1872, *Dingl. poly. J.*, **205**, 137; *Allen's Com. Org. Anal.*, **2**, 212.

two hours, so that saponification should have been complete; yet the difficulty might lie here, for R. Benedikt and K. Mangold* say that this method is attended with the disadvantage of saponifying some kinds of wax with diffi-

Serial Number.	Melting Point.	Specific Gravity at 15° C.	Acid Number.	Ether Number.	Total.	Ratio.	Cerotic Acid.	Myricin.	Total.	Ratio.	Iodine Number.	ADULTERANTS.	DESCRIPTION.
1	64·41	·9600	20·30	74·20	94·50	3·650	14·86	89·57	104·43	6·028	8·35	—	Pure Yellow Wax.
2	62·81	·9608	29·40	70·00	99·40	2·410	21·52	84·50	106·02	3·92	9·31	Stearic Acid.	" "
3	63·20	·9602	18·20	65·80	84·00	3·614	13·32	89·57	102·89	6·731	8·50	—	" "
4	63·80	·9624	20·30	77·00	97·30	3·788	14·80	92·95	107·81	6·547	8·71	—	" "
5	54·42	·9120	14·70	45·59	60·29	3·101	10·76	45·63	56·39	4·240	5·63	Paraffin.	" "
6	6[illegible]·81	·9641	19·60	75·60	95·20	3·857	14·35	91·26	105·61	6·352	7·26	—	" "
7	63·43	·9630	20·10	74·20	94·30	3·681	14·85	89·5	104·42	6·028	6·80	—	Pure Bleached Wax.
8	64·44	·9710	20·30	77·00	97·30	3·788	14·86	92·95	107·81	6·193	6·30	—	" "
9	62·22	·9690	19·60	65·80	85·40	3·357	13·35	76·93	90·28	5·755	9·80	—	" "
10	60·00	·9420	26·20	59·50	85·70	2·260	18·45	71·82	90·27	3·892	11·10	Paraffin, Stearic Acid.	Pure Yellow Wax.
11	63·00	·9620	18·04	74·49	92·53	4·132	13·16	89·95	103·11	6·821	8·70	—	" "
12	63·10	·9581	29·40	71·40	100·80	2·430	21·52	86·19	108·71	4·00	9·66	Stearic Acid.	" "
13	59·00	·9431	17·50	71·35	88·85	4·010	12·81	87·03	99·84	6·890	7·00	Paraffin.	" "
14	64·41	·9581	17·50	67·20	84·70	3·842	12·81	81·12	93·93	6·254	13·10	Paraffin, Rosin;	Manufacturing Wax.
15	62·45	·9500	18·91	71·51	90·42	3·776	13·83	86·33	100·16	6·232	9·11	Paraffin.	Pure Unbleached Wax.
16	63·76	·9520	20·30	74·20	94·50	3·655	14·86	89·57	104·43	6·027	7·42	—	" "
17	62·81	·9690	21·70	81·90	103·61	3·772	15·89	98·86	114·75	6·221	4·31	Probably Japan Wax.	Pure Bleached Wax.

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* 1891, *Chem. Ztg.*, **15**, 474.

culty. These investigators base their results on what they call "*aufgeschlossenes Wachs.*"

In view of the facts that some wax saponifies with difficulty, that no adulterant was found and that the remaining data were approximately normal, these waxes claim a position among the unadulterated.

Samples Nos. 2 and 12 contain stearic acid or an equivalent, yet the specific gravity and the melting point conform in each case as nearly to those of pure wax as could be required. How the manufacturer succeeded in doing this is a question for us to solve.

Heintz* has shown that by mixing stearic and palmetic acids in different proportions a melting point, varying from 69°·2 C. to 55°·1 C., can be secured. Was it a mixture of this kind? The writer was unable to decide.

The use of stearic acid, as an adulterant for beeswax, must be of comparatively recent date, for Hassel, who generally enumerates every conceivable adulterant, in his admirable work, does not allude to it, and Allen, in his *Commercial Organic Analysis*, **2,** 213, says it is "less frequently employed than some of the other adulterants."

The above results show, and other recent investigations corroborate it, that stearic acid is employed almost as extensively as any other adulterant.

Rosin was found only in the sample, designated "manufacturing wax."

Indications point to the presence of Japan wax in No. 17, but nothing definite could be ascertained, owing to the present inefficient methods at our disposal.

Below is a table embodying the properties of the various substances employed in adulterating beeswax. A few of the data are those of the writer, but the majority were secured from various sources in literature.†

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* *Ann der Physik.*, **92,** 588; Dragendorff's *Plant Analysis*, 1884, Eng. ed., p. 15.

† 1882, Dieterich, *Arch. der Pharm.* (3), **20,** 454. 1885, O. Dammer, *Illustriertes Lexicon der Verfälschungen*, etc. 1891, A. and P. Busine, *Bull. Soc. Chim.* (3), **5,** 654. R. Benedikt, *Analyse der Fette und Wachsarten, Zweite Auf.*, 311, *et seq.*

Substance.	Melting Point.	15° C. Specific Gravity.	Acids Soluble in Water.	Acid Number.	Ether Number.	Total.	Iodine fixed by 1 Gram of Wax.	Volume of Hydrogen at 0° C. and 760 mm. pressure given per gram.	Hydrocarbons from 1 Gram of Wax.
Yellow beeswax, . . .	62–64	·961– ·964	0–1	19–21	73–76	91–97	8–11	53–57·5	12·5–14·5
Beeswax bleached by various agents, . . .	63–64	·960– ·973	0–2	19–23	74–84·29	93–107·7	1·08–11·36	51–57	11–14·30
Cacao butter, ...	30–33	·945– ·982	0	0–3	192–200	192–204	34	—	—
Carnaüba wax, ...	83–84	·999	0	4–6	75–76	79–82	7–9	73–76	1·6
China wax, ...	53·5	·970	2	22	196	218	6·85	72·3	0
Japan wax, ...	47–54	·975	2	18–28	194–198	216–222	6– 7·55	69–71	0
Mineral wax, ...	60–80	·918– ·952	0	0	0	0	0– 0·6	0	100
Paraffin, ...	38–74	·913– ·914	0	0	0	0	17–31	0	100
Resin, ...	53·5	1·104–1·108	0	168	10	178	135·6	35	0
Spermaceti, ...	40–50	·945– ·96	0	0–2	136–142	136–144	—	—	—
Stearic acid, ...	53·5–69·2	·901–1·00	0	204	5	209	2–4	0	0
Suint wax, ...	62–66	—	0	95–115	4–7	102–119	13–18·5	0	14–18
Tallow, ...	42–50·5	·952– ·96	0	2·75–5	19[illegible]–208	196–213	27–40	52–60	0
Vegetable wax, ...	47–55·6	·947	2	17–19	200–210	218–220	6·6–8·2	73–74	0

GENERAL CONCLUSIONS.

Beeswax, in our markets, is adulterated to the extent of fifty per cent. while in the English markets the amount of adulteration rises to sixty-six and two-thirds per cent.

The melting point of beeswax varies from 62° to 64° C. It is raised by adding carnaüba wax, stearic acid, certain mineral waxes and paraffins China wax, Japan wax, cacao butter, resin, tallow, spermaceti, vegetable wax, certain stearic acids and paraffins, lower it, while it is apparently unaltered when adulterated with suint wax, certain mineral waxes, paraffins and stearic acid.

Beeswax varies in specific gravity from ·960 to ·973 and appears to be greatly influenced only by resin, carnaüba wax and certain mineral waxes, which increase it, and by paraffin, which lowers it.

The "acid number" ranges from nineteen to twenty-one milligrams of potash per gram of beeswax. Stearic acid, resin and suint wax increase, while carnaüba wax, mineral wax, cacao butter, paraffin and spermaceti decrease the acid number. China wax, Japan wax and vegetable wax do not vitiate the number seriously.

The "ether numbers" varying from seventy-three to seventy-six milligrams of potash per gram of beeswax, are unaffected by adding carnaüba wax; but China wax, Japan wax, cacao butter, tallow, vegetable wax increase it. Mineral wax, paraffin, resin, stearic acid and suint wax decrease it. It must be noted that wax bleached by certain chemical agents may have an ether number as high as eighty-four and yet be pure.

The percentage of iodine varies from eight to eleven, yet wax bleached by certain agents, as chlorine, may vary far from these percentages. Paraffin, mineral waxes and stearic acid lower the percentage, but cacao butter, resin, suint wax and tallow increase it. China wax, carnaüba wax, Japan wax and vegetable wax pass the prescribed limits but very little.

The volume (53· to 57·5 cubic centimetres) of hydrogen evolved from one gram of beeswax and the percentage (12·5 to 14·5) of hydrocarbons evidently are the most reliable data securable; the former being vitiated by all adulterants except tallow, and the latter by all except suint wax.

LABORATORY, SMITH, KLINE & FRENCH COMPANY,
PHILADELPHIA, PA.

COMMENTS ON THE DETERMINATION OF PHOSPHORIC ACID BY TITRATION OF THE "YELLOW PRECIPITATE" AS DESCRIBED BY MR. HENRY PEMBERTON, JR.

BY W. J. WILLIAMS, F.I.C., F.C.S., etc.

[*Read at the stated meeting of the Section, held November 21, 1893.*]

On September 19, 1893, at a meeting of the Chemical Section of the Franklin Institute, I heard with great interest Mr. Henry Pemberton's, Jr., paper on the determination of phosphoric acid by titration of the yellow precipitate with standard alkali.

For some time I have been seeking a *reliable* volumetric method for the determination of phosphoric acid. The well-known uranium nitrate method is sufficiently accurate for most purposes on an aqueous solution of phosphoric acid, but is entirely unreliable if the phosphatic material is dissolved in mineral acids or even in acetic acid.

After some conversation with Mr. Pemberton on the subject, subsequent to hearing his paper, he very kindly sent me by letter some valuable hints and instructions on the details of the process, with the help of which I began my investigation.

The first trials were made on ordinary mixed fertilizers, containing ammoniates and potash salts, and the result showed an almost exact agreement with previous results obtained by the usual gravimetric method.

	Phosphoric Acid by Pemberton's Vol. Method. Per Cent.	*Phosphoric Acid by Gravimetric Method. Per Cent.*	*Difference. Per Cent.*
Ammoniated phosphate, ...	15·475	15·480	0·005
Acid phosphate with ammonia and potash,	13·175	12·980	0·195
Acid phosphate with ammonia and potash,	13·730	13·820	0·090
Acid phosphate with ammonia and potash,	11·100	11·000	0·100

These I consider to be highly satisfactory results, and such as justified further investigation as to the reliability of the method on substances rich in phosphoric acid, such as Florida phosphate rocks, and on the other extreme of substances low in phosphoric acid, such as the "insolubles" in a well-made fertilizer.

High-grade Acid Phosphate.—Working on 0·2 gram for the "total phosphoric acid," and on 0·5 gram for the phosphoric acid "insoluble in ammonium citrate," I found

	By Volumetric Method.	*By Gravimetric.*	*Difference.*
"Total" No. 1, ...	16·830	16·57	0·26
No. 2, ...	16·750	16·89	0·14
"Insolubles" No. 1, ...	0·24	0·32	0·08
No. 2, ...	0·36	0·32	0·04

On ordinary mixed fertilizers.—

"Totals" No. 1, ...	15·28	14·78	0·50
No. 2, ...	14·60	14·14	0·46
No. 3, ...	12·29	11·45	0·84
No. 4, ...	13·83	13·43	0·40
"Insolubles" No. 1, ...	1·90	1·79	0·11
No. 2, ...	4·35	4·22	0·13
No. 3, ...	2·06	2·17	0·11
No. 4, ...	1·82	1·79	0·03

Here, again, I consider the results highly satisfactory.

I next worked on high grade Florida phosphate rocks, using in each case 0·1 gram of substance. To insure a fair sample, however, I first dissolved five grams of rocks in hydrochloric acid, and made up to 250 cubic centimeters and mixed thoroughly by shaking and decantation. Of this solution I took fifty cubic centimeters equal to one gram of rock, diluted to 250 cubic centimeters, and again mixed thoroughly by shaking and decantation. I then took twenty-five cubic centimeters of this second dilution equal to 0·1 gram rock, brought it to alkalinity with ammonia, and acidified with nitric acid, adding a little ammonium nitrate.

	By Volumetric Method.	*By Gravimetric.*	*Difference.*
Florida rock No. 1, ...	32·33	33·00	0·67
No. 2, ...	30·66	30·89	0 29
No. 3, ...	31·55	31·54	0·01
No. 4, ...	31·37	31·34	0·03
No. 5, ...	33·17	33·33	0·16
No. 6, ...	33·24	33·14	0·10

The greatest variation is in No. 1, where it reaches 0·67 per cent., but this is small compared with the variation in results from different analysts. For instance, No. 3 was analyzed by four chemists of repute, and the results were 31·54 per cent., 31·61 per cent., 31·86 per cent. and 34·56 per cent. The chemist who reported 34·56 per cent. was requested to revise his figures and reported the second time 34·44 per cent. These show a greater divergence from the results of the three first analysts than is found in the case of No. 1.

I think, therefore, that Mr. Pemberton's method followed carefully according to his instructions is entirely reliable, for high grade rocks, for plain acid phosphates and for mixed fertilizers, in the hands of careful and competent analysts. But with careless or unskilful manipulation the chances of serious error are very great. For instance, incomplete washing of the yellow precipitate would lead to very serious errors and misleading results but in careful hands the method is accurate and reliable.

WILMINGTON, DEL., November 21, 1893.

COMPARISON OF PEMBERTON'S METHOD OF PHOSPHORIC ACID DETERMINATION WITH THE OFFICIAL METHOD.

BY FRANCIS BERGAMI.

By the kindness of Dr. Terne, I came into the possession of a copy of Mr. Pemberton's paper, on "Phosphoric Acid Determination." The results shown therein indicate such a surprising accuracy of the method that Dr. Terne requested me to start an investigation at once, as it would be of the highest importance for our work to find a more rapid (and at the same time, equally accurate) process of phosphoric acid determination than the official method. As my spare time is very limited, I have extended my tests only to such materials as just at present enter our laboratory for examination. These materials consist mostly of ammoniated and mixed phosphates.

The results of all the tests made up to this time are given in the following table:

PHOSPHORIC ACID.

SAMPLE.	Official Method.	Pemberton Method.	Difference.
(1) Ammoniated phosphate,	11·84	11·68	0·16
	—	11·77	0·07
(2) Ammoniated phosphate,	13·20	13·05	0·15
	—	13·14	0·06
(3) Ammoniated phosphate,	8·80	8·68	0·12
(4) Ammoniated phosphate,	8·74	8·74	—
(5) Dissolved bone-black,	20·68	20·56	0·12
(6) { Ammoniated phosphate,	—	10·93 }	0·03
{ Water-soluble, phosphoric acid,	10·96	10·84 }	0·12
(7) Ammoniated phosphate,	12·48	12·35	0·13
(8) Dissolved bone-black, not identical with No. 5,	20·68	20·55	0·13
(9) Acidulated S. C. Rock:			
Total phosphoric acid,	15·52	15·34	0·18
Insoluble phosphoric acid,	1·72	1·68	0·04
Available phosphoric acid,	13·80	13·66	0·14
(10) Ammoniated phosphate,	12·32	12·17	0·15
(11) { Ammoniated phosphate,	—	—	—
{ Water-soluble, phosphoric acid,	10·56	10·47	0·09
(12) Acidulated S. C. Rock:			
Total phosphoric acid,	15·29	15·15	0·13
Insoluble phosphoric acid,	2·56	2·49	0·07
Available phosphoric acid,	12·73	12·67	0·06
(13) Refuse bone-black,	34·40	34·03	0·37
	—	33·94	0·46
	—	34·03	0·37
(14) South Carolina rock,	27·66	27·34	0·32
(15) Florida rock,	32·24	31·94	0·30

In reviewing all the results, it can be seen that, on the average, the Pemberton process gives slightly lower results than the official method. Assuming my work to be as free from individual error as careful work can be, there are only two explanations for the differences: either the results of the official method are a little too high, or those of the Pemberton method are a little too low. I feel very much inclined to accept the first explanation, for the following reason:

It has been repeatedly stated by different chemists that it is hardly possible to obtain by one precipitation a precipitate of ammonium-magnesium phosphate absolutely free from magnesium oxide, and it has been recommended to dissolve the precipitate again and re-precipitate it with ammonia.

Dr. N. von Lorenz has only lately published his investigation in regard to this source of error in the official method (*Fresenius Zeitschrift*, 1893, p. 64). He shows that addition of about two per cent. of citric acid to the solution of the phosphomolybdate in ammonia will prevent any contamination by magnesium oxide.

When I had obtained the results on Sample No. 13, a refuse bone-black, I found the difference between the official test and even the highest result of the Pemberton method, namely, 0·37 per cent., too high to be passed without any closer consideration. In this case, I had accidentally omitted the neutralization of the ammoniacal solution of the phosphomolybdate by hydrochloric acid. Therefore, the idea struck me that this neglect might be the cause of too high a result, and I concluded to repeat the test twice with addition of citric acid, as recommended by Dr. von Lorenz.

The results thus obtained were 34·08 per cent. and 34·16 per cent. against 34·03 per cent. and 33·94 per cent. by Pemberton method and 34·40 per cent. by official method without neutralization. In former years, I had always precipitated without previous neutralization of the ammonia solution, but as I have lately followed strictly the official way and neutralized, I thought surely that the omission of neutralization was the cause of the high result. The smaller differences in all previous tests could easily be explained as individual working errors, but when I obtained the results in Samples 14 and 15, I felt a little astonished.

In these cases, I was sure of no neglect on my side, the official way was carefully carried out as in all other samples, and I had made the solutions of the yellow precipitate as nearly neutral as possible. Still, the differences between both methods were 0·30 per cent. and 0·32 per cent., respectively.

I always wash the ammonium-magnesium phosphate until the filtrate shows no chlorine reaction, so that the source of error arising from incomplete washing is absolutely excluded, and I am, therefore, at a loss to find any other explanation for the differences than that, even in nearly neutralized solutions, a small amount of magnesium oxide is thrown down, together with the ammonium-magnesium phosphate, and renders the results of the official method too high. Naturally, the error will show itself more in high-grade phosphates, than in those with lower percentage.

In calculating the results, I used the figures obtained by Mr. Pemberton, which are based upon the fact that twenty-three molecules of alkali are necessary to neutralize one molecule of ammonium phosphomolybdate. In establishing this fact, Mr. Pemberton precipitates a solution of di-sodic hydric phosphate by magnesium mixture, but he obtains a precipitate absolutely free from magnesium oxide by taking the precaution to dissolve the first precipitate again and re-precipitate with ammonia.

In this way he eliminates the above stated error in the official method.

If, in establishing the relation between the phosphoric acid in the yellow precipitate and the standard alkali solution, the ammonium-magnesium phosphate were weighed directly after the first precipitation, I feel almost sure the figures thus obtained would be higher, and that results in analyses calculated on those figures would not show such large differences from the official method, as they would involve the same source of error.

In regard to the execution of the Pemberton method, I should like to state the following:

Extremely great care must be taken in washing the yellow precipitate until free from acid. Testing with delicate litmus paper should never be omitted. In regard to rapidity, I found it of some advantage to introduce a little change in Mr. Pemberton's mode of procedure.

To the twenty-five cubic centimeters of acid solution, which is always obtained in the same way (one grain substance thirty-five cubic centimeters nitric acid and five cubic centimeters of hydrochloric acid), I add at once ten cubic centimeters of strong ammonia (specific gravity 0·90), and, after a little stirring, fifteen cubic centimeters of nitric acid (specific gravity 1·42).

This operation secures about the same conditions for all tests, and produces at the same time a temperature of 75° to 80° C., which reduces the time required for heating to boiling point to a minimum.

The method is absolutely free from all difficult manipulations, and the only inconvenience I experienced with it occurred in such samples as gave dark colored acid solutions.

A considerable part of the coloring matter enters the precipitate and imparts to the solution in alkali a brownish color.

This renders the titration a little difficult, and may, in some cases, give rise to uncertainty and error. A previous ignition of the sample or treating with concentrated sulphuric acid would overcome this difficulty. Whether in the case of solution in sulphuric acid, a larger amount of nitrate of ammonia and a longer allowance of time for complete precipitation would be necessary, is still an open question and needs investigation.

Mr. Pemberton recommends a standard alkali solution, which is free from carbonic acid. I have found that in the determination of nitrogen and ammonia a solution with a small amount of carbonates works just as well, as if free from the same, provided phenolphthalein and cochineal are used as indicators for standardization and analysis, respectively. Both indicators show absolutely sharp end reactions, even if a small amount of carbonates is present. Curious of seeing if carbonic acid would have any detrimental effect in this special case, I repeated some of the tests with an old soda solution, containing some carbonates, with the following results:

SAMPLE.	*1*	*4*	*5*	*12*	*15*
Alkali with CO_2, ...	11·68	8·69	20·47	15·07	31·94
Alkali without CO_2, ...	11·77 11·68	8·74	20·56	15·16	31·94

The close agreement of the different results seems to show that the precipitation of the carbonic acid is an unnecessary precaution.

I do not consider the number of tests made sufficient to prove the absolute infallibility of the Pemberton method, but I think that my work shows at least the probability of obtaining fair results by the same.

The results obtained by Mr. Pemberton and myself should be encouraging enough for any chemist employed in the control of fertilizers, to make a careful study of the method, with the hope of producing an absolute proof of accuracy, which would justify the abandonment of the old, tedious and time-wasting procedure of the official method.

NORMAL CHLORINE IN SPRING WATERS NEAR PHILADELPHIA.

By Reuben Haines.

The term "normal chlorine" is used to designate the amount of chlorine naturally existing in waters that are entirely free from all contaminating influences arising from the life and occupations of man.

Not only waters directly polluted by this means are to be excluded, but also those in which the ground water within their drainage area has been contaminated. It is necessary, therefore, to obtain the water from near its source and to ascertain that within its watershed there exists nothing likely to affect the chemical character of the water. In a very sparsely inhabited region comprising large tracts of forests and uncultivated land such normal waters would not be difficult to find. It is quite otherwise in fertile agricultural districts in the vicinity of cities and towns.

It appears probable that in most instances the natural or normal chlorine of a particular locality will be found a tolerably constant average, although wide variations are found occasionally in single cases. This has been found true in Massachusetts, where this matter has been under investigation for several years.

As chlorine is one of the most important factors in water analysis for determining the potability of a water and is by reason of its permanence in the form of sodium chloride well adapted for the relative measurement of pollution, it is desirable to know the amount which is normal for a particular locality.

It should be stated, however, that the question of potability is not necessarily considered in the selection of these normal waters. Thus many swamp waters although very highly colored and containing large amounts of vegetable matter are quite suitable for this purpose. While on the other hand many spring waters which receive ground water draining from farm-land are sufficiently pure for domestic use, but are for this reason, viz:—the character of the ground water—not to be classed as normal waters.

Special geological features of rock or soil, however, may greatly affect the chlorine content of waters in certain districts so far as to render the determination of chlorine of little value for this purpose. In the vicinity of the sea-coast a considerable increase in chlorine is to be expected, which, except in immediate proximity to salt marshes and within the line of highest tides, is probably due to salt spray carried inland by winds and precipitated with the rain.

Investigations in Massachusets (*Report of State Board of Health on Examination of Water Supplies and Inland Waters*, 1890) have shown that the normal chlorine decreases in quite regular series from the coast to the central part of the State. Normal waters near the coast contain about 0·65 part chlorine per 100,000 and in the western part of the State less than 0·10 part. Lines called "isochlors" are drawn on a map of the State, connecting localities having equal amounts of normal chlorine, and these "isochlors" have a general parallelism to the coast line. It appears reasonable to attribute the gradual decrease of normal chlorine to the diminishing influence of sea-air.

From some recent investigations I have made, I believe, a somewhat similar series for normal chlorine can be found for New Jersey and Eastern Pennsylvania. In the present paper, the vicinity of Philadelphia, west of the Delaware River, is alone under consideration. It has, however, been quite difficult to find sources of water in this district which would reasonably satisfy the necessary conditions. Springs on a wooded hillside were mostly selected.

Ten springs, of which twenty-one samples were taken at different times during the year 1893, were found to be available for the purpose and distributed as follows:

Five springs located on or near the line of the Philadelphia and Newtown Railroad, of which eight samples were taken. Four springs in Chester County, of which there were six samples. One spring on the Wissahickon Creek, Fairmount Park, seven samples taken almost monthly, from April to October.

The results are given as follows, stated in parts per 100,000:

NEWTOWN RAILROAD FROM HARPER'S TO PAPER MILL STATION.

Number of Spring.	*I.*	*II.*	*III.*	*IV.*	*V.*
First sample,	·27	·26	·24	·27	·23
Second sample,	—	·283	·245	·256	—
Average,	·27	·271	·242	·263	·23

CHESTER COUNTY, PA.

Location.	*Cedar Hollow.*	*White Horse Road.*	*Dalesford.*	*Malvern.*
First sample,	·210	·190	·170	·240
Second sample,	·180	—	·256	—*
Average,	·195	·190	·213	·240

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* A second sample of this spring, taken five months after the first, was rejected, because a large increase in nitrates, as well as increase in chlorine, showed some pollution to have taken place between these periods. The amount of nitrates in the first sample, collected May 30th, was ·072 parts per 100,000.

WISSAHICKON PARK DRIVE, SPRING ABOUT 400 YARDS ABOVE RITTENHOUSE LANE.

Seven samples collected from April 12 to October 9, 1893:

Number of Sample.	*I.*	*II.*	*III.*	*IV.*	*V.*	*VI.*	*VII.*
Chlorine,	·16	·15	·22	·22	·214	·183	·207

Average of these seven samples, ... ·193

In four of these samples the nitrates were determined giving a maximum of ·10 minimum ·08 and average ·087 parts per 100,000. A determination of ammonia gave no free ammonia and an exceedingly small amount of albuminoid ammonia.

The average chlorine for the series is ·231 parts per 100,000.

It is probable that the results from the spring at Cedar Hollow and the one on the Wissahickon represent most nearly the true normal, since three of the others are possibly influenced by the cultivation of land or by pasturage in their vicinity. The spring at Cedar Hollow gave only faint traces of nitrates in 100 cubic centimeters of water. The condition and environment of this spring were very good. It flows rapidly from the base of a steep hill covered with dense woods. Of the springs, near the Newtown Railroad, the second gave nitrogen in the form of nitrates ·05 parts per 100,000, and the fifth no nitrates.

It is probable, therefore, that the normal chlorine for the vicinity of Philadelphia approximates closely to ·20 parts per 100,000, and presumably rather under than over this amount. Additional analysis of these and other springs are desirable in order to fix the limit more definitely.

The chlorine was determined by the usual volumetric method with silver nitrate and potassium chromate, but with the improvements and corrections described by Hazen (*Amer. Chem. Jour.*, xi, 409). As this improved method may not be familiar, except to those making similar investigations, it may be briefly stated here as follows: 200–250 cubic centimeters of the water to which are added fifteen to twenty milligrams sodium carbonate are evaporated in a porcelain dish to about twenty-five cubic centimeters. Wash down sides of dish with distilled water, using a rubber, until the volume approximates fifty cubic centimeters. When cold, add one cubic centimeter potassium chromate solution containing sixty milligrams chromate per cubic centimeter. Titrate with silver solution equivalent to 0·5 milligram chlorine per cubic centimeter until a faint permanent tint is visible. From the result of titration deduct a correction for volume represented by the formula

$$X = \cdot003\ V + \cdot02$$

in which V is the volume of the liquid in cubic centimeters at the end of the titration. The silver nitrate solution is also corrected previously in making up the solution by the addition of one per cent. of the theoretical weight of silver nitrate required; or standardize with sodium chloride solution and apply the above correction for volume, which will give the same strength of solution. In colored waters from swamps or peaty waters the coloring matter is, previously to evaporation precipitated by alumina hydrate, or by aluminum sulphate and sodium carbonate. The solid residue in a platinum dish after ignition by Drown's radiator may also be used for the determination of chlorine, if previous to evaporation, fifteen to twenty milligrams of sodium carbonate have been added to the water. I have found duplicates to agree very exactly when using this residue after ignition and have found close agreement between all three methods of getting rid of the vegetable coloring matter in natural waters, as described by Hazen. When using aluminum sulphate it is best to perform the titration with silver nitrate by gaslight.

A CONTRIBUTION TO PEMBERTON'S VOLUMETRIC METHOD FOR PHOSPHORIC ACID DETERMINATION.

BY DR. BRUNO TERNE.

[*Read at the stated meeting of the Section, held December 19, 1893.*]

On September 19, 1893, Mr. Pemberton, Jr., presented to the Section, a paper on the "Determination of Phosphoric Acid by the Filtration of the Yellow Precipitate with Standard Alkali."

The results obtained by Mr. Pemberton were such, that it appeared to us, at once, the results of this investigation should be taken up by the chemists interested in the determination of phosphoric acid.

At my request, Mr. Francis Bergami, for the last seven years in charge of the analytical control work of the factory of the Baugh & Sons Company, undertook to make a comparison of the Pemberton method with the official gravimetric method.

Mr. Bergami has made such comparison in fifteen different samples. The first twelve samples represent market products of the fertilizer trade; the last three samples, of raw material for the manufacture of the first.

The highest difference between the two methods, in the first twelve samples, is 0·16 per cent.

If you take up my paper read before the Section, October 18, 1892, pp. 9 to 12, and compare the differences which the official chemists have made on the test sample, you will find that the differences between the official and the Pemberton method, as obtained by Mr. Bergami, are insignificant.

In the last report issued by the Agricultural Department, of the meeting held in Chicago, August 24 to 26, 1893 (*Bulletin* 38), we find on p. 8, determinations of citrate insoluble phosphoric acid made by seventeen different chemists, with results of:

Highest. *Per Cent.*	*Lowest.* *Per Cent.*	*Differences.* *Per Cent.*
1·69	1·33	0·36
2·11	1·03	1 08

while Mr. Bergami, in Samples 9 and 12 in the citrate insoluble phosphoric acid between the official and the Pemberton method, found only differences of 0·04 and 0·07 per cent.

Taking the results of the last three samples with high percentage of phosphoric acid, the highest difference obtained between the two methods, is 0·46 per cent.

Compare this, with the results of the test samples in 1892 for total phosphoric acid by the official method, and you find recorded 0·46 per cent., 1·28 per cent., 1·50 per cent., 1·45 per cent.

While the samples 13, 14 and 15 of Mr. Bergami show, as the highest, 0·46 per cent., the last official record we have on total phosphoric acid, give the same figure, as the lowest difference.

The volumetric method, as proposed by Mr. Pemberton, is, in my judgment, as reliable as the official method, and, if anything, more correct in the results.

A great advantage for a laboratory, is the time-saving of this method, without any loss of accuracy.

The work, that Mr. Bergami lays before you, has been done with the utmost care and critical observation of all possible shortcomings of the new method.

I am so satisfied with the results obtained, that I do not hesitate a moment to adopt the Pemberton volumetric method for the control of our factory work, though samples of shipments must be treated according to the adopted rules of the association.

This volumetric method of determining phosphoric acid is, to my mind, of such value to all chemists interested in phosphoric acid determination, and principally to the station chemists and fertilizer manufacturers, that a united effort should be made to push the adoption of the same, at least as an alternate method, before the Association of Official Agricultural Chemists.

I know that Mr. Williams, of Walton Whann & Co., at the next meeting, as indicated in the communication he sent to the Section, will join in this movement.

I shall endeavor to bring this matter prominently before the next meeting of the association, and in the meantime I am trying to interest the leading members of the association in the very excellent method of our fellow-member, Mr. Pemberton.

REPORT OF THE CHEMICAL SECTION.

(For the year 1893.)

JANUARY 1, 1894.

Mr. Joseph M. Wilson, President of the Franklin Institute:

SIR:—I have the honor to submit the following report of the proceedings of the Chemical Section for the year 1893:

The interest of members in the welfare and progress of the Section has never been greater than that shown at the present time, and as demonstrated by the list of original papers and communications herewith submitted, much has been accomplished during the year in the way of research in the fields of pure and applied chemistry.

The officers for the year have been as follows:

President,	DR. WM. H. GREENE.
Vice-Presidents,	MR. HENRY BOWER, DR. D. K. TUTTLE.
Secretary,	DR. WM. C. DAY.
Treasurer,	DR. H. W. JAYNE.
Conservator,	DR. WM. H. WAHL.

Stated meetings, ten in number, have been held as required by the by-laws. In addition to these a special meeting was held on June 8th, for the purpose of having a lecture by Dr. Ernest Mailliau, Director of the Government Testing Laboratory, at Marseilles, France, on the "Methods of Testing Fats and Oils." This lecture has been published in the *Journal of the Institute* as a part of the Section's proceedings.

Membership.—The number of members on the Treasurer's books at the beginning of the year was seventy-six. Since that time seven new members have been elected, one has resigned, two have died, and four have been dropped for non-payment of dues, thus making the present membership seventy-six.

Finances.—The Treasurer's Report shows cash on hand at the beginning of the year $74.16, receipts during the year $141; expenditures, $187.64, thus leaving a balance of $27.52 in the treasury at the present time.

The following is a list of the papers which have been read before the Section at its regular and special meetings. The papers are given in the order of their presentation:

"A New Process for the Production of Manganese on the Commercial Scale," by Dr. Wm. H. Greene and Dr. Wm. H. Wahl.

"Artesian Wells," by Prof. O. C. S. Carter.

"Phenolphthalein and Methylorange," by Dr. E. H. Keiser and Mary Bidwell Breed.

"Report on Results Obtained in the Field of Stereochemistry," by Mr. S. W. Young.

"A New Method of Reducing Metallic Oxides," by Dr. Wm. H. Wahl and Dr. Wm. H. Greene.

"The Action of the Haloid Acids in Gas Form upon Molybdic Acid," by Dr. E. F. Smith and Mr. Vickers Oberholtzer.

"A Process of Treating Mixtures Containing Sulphides of Precious Metals and Copper," by Dr. D. K. Tuttle.

"The Action of Ammonia Gas upon Molybdenyl Chloride," by Dr. E. F. Smith and Mr. Victor Lenher.

"Report on Recent Contributions to our Knowledge of Metallic Reducing Agents," by Dr. H. F. Keller.

"The Methods of Testing Fats and Oils," by Dr. Ernest Mailliau.

"The Rational Utilization of City Garbage," by Dr. Bruno Terne.

"Gelatinous Silver Cyanide," by Mr. Lee K. Frankel.

"The Determination of Phosphoric Acid by the Titration of the Yellow Precipitate with Standard Alkali," by Mr. H. Pemberton, Jr.

"The Atomic Weight of Molybdenum," by Dr. E. H. Smith and Mr. Philip Maas.

"The Azines of the Lapachol Group," by Dr. S. C. Hooker.

"The Change from Ortho- to Para- and from Para- to Ortho-Quinones," by Dr. S. C. Hooker and Wm. C. Carnell.

"Experiments on Slag Cements," by Mr. R. W. Mahon.

"Notes on the Examination of Beeswax," by Mr. L. F. Kebler.

"The Availability of Nitrogen in Mixed Fertilizers," by Dr. Bruno Terne.

"Contribution to Pemberton's Volumetric Method for Phosphoric Acid Determination," by Dr. Bruno Terne.

"Comparison of Pemberton's Method of Phosphoric Acid Determination with the Official Method," by Mr. Francis Bergami.

"Normal Chlorine in Spring Waters near Philadelphia," by Mr. Reuben Haines.

Respectfully submitted,
Wm. C. Day, *Secretary.*

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